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Optical control of alignment and patterning in an azobenzene liquid crystal photoresist[†]

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This report describes a liquid crystalline material that can be cured and patterned with green light and photoaligned with blue light. The liquid crystalline material consists of azobenzene repeat units that undergo photoisomerization between *trans* and *cis* isomers when irradiated with UV and visible light. A formulation containing an azobenzene diacrylate mesogen was spin-coated and cured with green light through a photomask to generate a patterned film. Unexposed regions of the film were rinsed away. Exposure of the pattern to UV light to generate a *cis* enriched film greatly enhances the film's propensity to photoalign when exposed to polarized blue light. The orientations of the mesogenic repeat units are characterized with polarized UV-Vis spectroscopy and birefringence measurements. Photochemical switching between *cis* and *trans* conformations of the azobenzene chromophore is characterized with UV-Vis spectroscopy.

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Introduction

Achieving spatial and orientational control of smart materials remains critical towards facilitating the design and application of next-generation micro and nanoscale devices.^{1–5} Liquid crystal polymers (LCPs) are one such material that can exploit collective molecular-level motion to manifest macroscopic dimensional and optical changes^{6–8} for a variety of applications including micro-actuation, sensing, and flat optics. However, they are unique in comparison to most other polymers utilized in microfabrication in that they demand both control of their patterning and their crystalline orientation to be optimally incorporated into device designs. Achieving a single chemical blend that can accommodate this dual control remains a challenge.

To date, most LCP chemical systems demand tackling each of these functions separately. Most meso and macroscale thick film LCP device demonstrations manually cut the material to accomplish patterning.^{9,10} For 2D microscale patterning there are several well-established methods suitable for polymers that can be extended to LCPs, including various soft lithography techniques¹¹ (*e.g.* nanoimprinting), dip pen lithography,¹² and

drying induced self-assembly for custom geometries.¹³ Methods that utilize light to pattern surface features are of particular interest because light provides a simple, clean and non-invasive stimulus for manipulating matter.^{14,15} Traditional ultraviolet (UV) photolithographic based indirect subtractive LCP patterning may be possible in conjunction with plasma etching, however incorporating an appropriate mask material that can be both deposited and sacrificially removed without impacting the material quality or alignment is a challenge and this approach does not appear to have been presented in the literature. Direct UV photolithography of an LCP was demonstrated by Yamashita et al.,¹⁶ however the yield was limited and optimal crosslinking required elevated temperature. Sousa et al.17 reported mixed 2D control of a cholesteric LCP's chiral nematic and isotropic regions using UV photomasking in concert with an underlying polyimide alignment layer, but this work did not include any form of controlled spatial patterning or removal of the film. Direct laser writing (DLW) patterning has been shown as a means of 3D patterning in a liquid crystal polymer by multiple groups with varying levels of sophistication,18-20 however this method lacks extensibility to wafer scale batch fabrication.

Alignment of LCP anisotropic orientation has often been demonstrated by utilizing mechanical alignment sublayers onto which an LCP is molded or deposited on the surface. This was preceded by work that involved mechanical rubbing to create nanoscale striations but has been supplanted by more deliberately engineered methods including a surface alignment grating and scaffolding structures fabricated *via* DLW or nanoimprinting.^{21–24} Simpler, non-invasive, and more extensible photoalignment procedures that expose LCs to linearly

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polarized light to induce anisotropy have been widely reported as well.^{25–28}

Key to controlling liquid crystal alignment with photons is the incorporation of molecular photoswitches, a number of which have provided important light-responsive building blocks to effect reversible changes in soft materials.²⁹⁻³⁴ Among the various photoswitchable molecules employed, azobenzene chromophores are among the most explored in terms of demonstrating reversible molecular and macroscopic changes in materials when irradiated with UV and visible light in a large variety of synthetic and biological materials.³⁵⁻³⁹ Azobenzene undergoes trans-cis photoisomerization when irradiated with UV and visible light. In general, irradiation of the linear trans isomer with UV light results in the formation of the bent cis isomer. The cis isomer is metastable and relaxes back to stable trans isomer either thermally in the dark or through exposure to visible light. The ideal irradiation wavelengths and the ratio of trans to cis isomers after irradiation depend on the absorption spectra and the extinction coefficients of the two geometries. An important consequence of the capability of azobenzene to access two different molecular conformations is that the liquid crystallinity of azobenzene-based materials can be controlled with photons. The linear trans geometry is liquid crystalline, whereas the bent cis geometry is not. UV irradiation of a trans-azobenzene liquid crystalline material can induce an order-disorder transition of the liquid crystal medium. However, exposing the disordered azobenzene system to linearly polarized light at a wavelength both isomers absorb induces a trans-cis-trans reorientation in which the azobenzene chromophores are aligned in a direction perpendicular to the polarization axis of the light.40 While both trans-cis and cis-trans isomerization pathways are possible, the dichroic absorbance of trans-azobenzene to linearly polarized light results in a statistical build-up of the trans isomer oriented normal to the polarization axis of the incoming light.³¹ Many reports demonstrate that azobenzene-based liquid crystal systems can show observable photomechanical effects when photo-isomerized, converting molecular motion into macroscopic movement.41-49

In this report, we demonstrate an azobenzene-based liquid crystal polymer (Azo-LC) material that can be cured and photopatterned at the microscale with green light, photo-aligned so that chromophores are preferentially oriented in the same direction using a polarized blue laser, and photo-isomerized with UV and visible light. The patterning and photoalignment exposures are conducted at room temperature. The properties of the material allow for the fabrication of a patterned birefringent film without a pre-cast and oriented alignment layer. Photoreconfigurable Azo-LC thin polymer films can be used as a negative photoresist and can be used in applications where direct control of the orientation of the LCs is required. The motivation behind this work is the realization of an LCP chemistry that can be deposited using conventional spin or spray deposition found in most microfabrication facilities and then be both photoaligned and photopatterned upon irradiation with polarized light and chemical solvent development, much like a traditional photoresist. Such a blend would both reduce microfabrication complexity associated with these materials and increase accessibility for novel microdevice design. Specific applications include soft robotics, liquid crystal sensing devices, polymeric optical lens and metasurfaces, and microelectromechanical systems (MEMS).^{9,10,50,51}

Results and discussion

The photopolymerizable and photo-alignable material described herein is based on 4,4'-bis(6-acryloyloxyhexyloxy)azobenzene, 1, which contains a photo-isomerizable azobenzene chromophore, flexible alkyl chains with six methylene units and two polymerizable acrylate moieties, as shown in Scheme 1. The acrylate endgroups on 1 allow the photo-switch to polymerize in the presence of radicals to form a crosslinked film. In general, crosslinking enhances thermal stability and solvent resistance in polymer thin films.⁵² Utilization of photo-initiators as the radical source for acrylate polymerization allows the reaction to be initiated and controlled with light in a spatially controlled manner, enabling photo-patterning. Azobenzene crosslinked films were prepared by first mixing the azobenzene diacrylate with pentane dithiol in the presence of catalytic amounts of triethyl amine and heating for 1 h at 65 °C. Acrylates can react with thiols via thiolacrylate Michael addition,⁵³ providing a facile route to increase the molecular weight of the diacrylate prior to photopolymerization, thereby improving processability into thin films via spin-coating and improving the thin film curability so that a continuous macroscopic network can be obtained with relative ease. After heating, trimethylolpropane tris(3-mercaptopropionate) was added, which facilitates cross-linking and surface cure during the photo-polymerization reaction through a free radical mediated thiol-ene reaction. Irgacure 784, which is a titaniumbased photo-initiator that can be activated with green light, was added and the mixture was dissolved in toluene and spin-coated onto a glass slide. Green light irradiation of spin-coated films results in an insoluble cross-linked network as depicted in Scheme 1. The azobenzene repeat units comprising the resulting network can be photo-isomerized between cis and trans geometries. After photo-generation of a film containing cis chromophores with UV light, irradiation with linearly polarized blue



Scheme 1 Schematic description of *trans-cis* isomerization, polymerization, crosslinking, writing and erasing procedures. The azobenzene subunits of the film can be reversibly isomerized between *cis* and *trans* isomers when irradiated with UV and visible light. The *cis* isomer can also revert thermally to the *trans* isomer. After photogeneration of the *cis* film, irradiation with polarized blue light photo-aligns the liquid crystalline chromophores into a monodomain nematic film.

light results in a photoaligned film in which the linear *trans* chromophores form a monodomain nematic liquid crystalline structure. The liquid crystalline state can be erased by irradiation with UV light and regenerated by re-exposure to linearly polarized blue light. The system can be repeatedly switched between the *trans* and *cis* isomers as well as liquid crystalline and isotropic structures.

Fig. 1 shows a schematic illustration of the photopolymerization and photopatterning process of azobenzene-functionalized LC thin films. Azobenzene films based on compound 1 were prepared by spin-coating a solution of the azobenzenecontaining formulation (10% by weight in toluene) on plasmacleaned glass or quartz slides. The films were then covered with a chromium on quartz photo-mask used in conventional optical lithography containing a pattern of opaque and transparent regions and exposed to green light for various amounts of time (Fig. 1). Green light that passes through the transparent regions of the photo-mask initiates a polymerization reaction that leads to an insoluble cross-linked network containing azobenzene repeat units. The opaque portions of the mask define the regions of the film that remain unchanged during the photolithographic patterning process and can be rinsed off with solvent, provided that the film is rinsed immediately after irradiation. After exposure to green light through a photo-mask, the films were rinsed with toluene to remove the unpolymerized portions of the film in the masked region, leaving a pattern of cured material on the substrate that is discernible by eye. Other rinsing attempts with acetone, methanol, isopropanol and water were ineffective at removing the masked film areas. The resulting patterned films are shown in Fig. 1 and indicate that photopatterning is

effective when irradiated for 10-60 s. The dark regions of the images contain no material and represent the opaque region of the photo-mask, showing that this blend behaves as a negative photoresist. Green light does not impinge upon the regions of the film that were concealed by the opaque sections of the photomask and as a result photopolymerization does not initiate in these masked regions. The light portions of the image represent photo-cured material and reproduce the shape of the transparent regions of the photo-mask where light was able to interact with the spin-coated film and initiate the radiation-induced curing reaction. The cured pattern is stable when placed in toluene for 24 h, however, only a brief rinse is required to wash away the portions of the film that were masked and hence not exposed to green light. The image of the 60 s exposed sample qualitatively shows that a subtle amount of material remains in the masked region, whereas the samples irradiated for 10-45 s qualitatively look more pristine. Note that when thiols are not present in both the pre-mix and the spin-coated film a pattern was not obtained after 60 s of exposure, signifying the importance of the thiol components for efficient photo-patterning. The glass transition temperature, T_{g} , of the material was measured with differential scanning calorimetry (DSC) and is in the range of 5-10 °C. The film thickness of samples irradiated for 10 and 30 s was measured with profilometry and showed a general range of 130-400 nm after rinsing of the exposed area (see S1, ESI[†]). The topography of the films was measured with confocal optical microscopy. The films show a grainy quality to the texture of the film which might be due to rinsing away lower molecular weight material. Further optimization of the curing process might entail manipulating the spin-coated film thickness,



Fig. 1 (a) Spin-coated films were masked and irradiated with monochromatic green light (532 nm). A photopolymerization reaction occurs in the regions of the film that were exposed to light. Rinsing with solvent removes material from the masked region of the film, leaving a pattern of polymerized material on the substrate. (b) Samples shown were irradiated for 1 s (top, left), 10 s (top, middle), 30 s (top, right), 45 s (bottom, left), 60 s (bottom, middle) and 5 min. (bottom, right). In general, exposure times of 10-45 s give the cleanest patterns. (c) UV-Vis analysis (right) shows that samples irradiated for 10, 30 and 45 s show detectable levels of signal when the irradiated portions of the surface are analyzed, and no signal when the masked regions are probed. The sample irradiated for 60 s shows material in the masked region after rinsing, however, the intensity is much higher when a region of the same substrate that was exposed to green light is examined.

realizing a less harsh rinse condition, changing the exposure conditions and modifying the weight percent of the formulation components.

UV-Vis spectroscopy was used to probe the efficiency of rinsing material from the masked regions of the pattern. UV-Vis spectra of the masked areas and the regions that were exposed to green light for 10-60 s are shown in Fig. 1c. For samples exposed to green light for 10-45 s, no detectable material was present in the masked region of the film, whereas the regions of the substrates that were exposed to green light show the characteristic band in the UV region of the spectrum at approximately 342 nm corresponding to the π - π * transition of the *trans* isomer of the azobenzene chromophore. The sample exposed to green light for 60 s shows that azobenzene material can be detected in the region of the film that was masked. The absorbance intensity in the masked region is approximately 0.3, however, the exposed region has an absorbance of approximately 0.85, indicating a much greater amount of material in the irradiated portions of the surface as expected. A relatively short exposure time of 1 s was found to be ineffective at generating a solvent stable cross-linked network. A cure time of five minutes resulted in an excessive amount of material in the masked region. This may be a result of over exposure from low levels of off-axis light. Additionally, curing in the masked area may be a result of a spontaneous dark reaction between the acrylate and pentaerythritol tris(mercaptopropionate), or a laterally propagating reaction after curing with green light is initiated.

Regardless of the mechanism, overexposure compromises the integrity of the pattern.

It is known that the shelf-life of acrylate-based formulations can be shortened when oligo-thiol derivatives are present. In some cases, films or pastes made from similar materials that were stored in the dark for a 24 h period were found to cure at room temperature. Given the time-dependent stability of the material, the time between spin-coating and curing was kept to a minimum in the experiments described herein. Typically, no more than 1 minute elapsed after spin-coating and before masking and exposing a spin-coated film to green light. When dissolved in toluene, formulations were stable for periods of greater than 1 month.

In addition to confirming the presence of azobenzene liquid crystal polymer after photo-patterning and rinsing, UV-Vis spectroscopy was also used to characterize the photochromic and structural properties of the photopolymerized films. Fig. 2 shows UV-Vis spectra before and after exposure to UV and visible light. The original spectrum of the film after spin-coating and exposure to green light to induce photopolymerization is shown. The spectrum contains the typical UV band at approximately 342 nm corresponding to the π - π * transition of the azobenzene chromophore.⁵⁴ When UV-Vis spectra of the initial film are measured with polarized light (0 and 90 degrees), the spectra overlap each other as well as the original spectrum and show no difference in intensity, indicating that the



Fig. 2 (a) The UV-Vis absorption spectrum of a film based on *trans*-**1** that was cured with green light is shown. Irradiation with UV light converts the *trans* isomers to *cis* isomers as indicated by the increase in absorbance in the 450 nm region. Irradiation with visible light regenerates the *trans* isomer as indicated by the attenuation of the band in the visible region. Several cycles of the photo-switching process can be completed without loss of photochromism and enhance the absorption intensity in the UV region (see inset). (b) After cycling between the *cis* and *trans* isomers, irradiation of the *cis* enriched film with polarized blue light results in significant dichroism. The intensity of the absorbance band in the UV region shows a significant difference when analyzed with light polarized at 0 and 90 degrees, indicating that the film is photoaligned and has a dichroic ratio of approximately 2.03.

azobenzene chromophores are randomly oriented during spincoating (see ESI[†] S2). Irradiation of the sample with UV light (365 nm LED) for 3 s induces trans-cis photoisomerization of the azobenzene chromophores, as shown by the reduction in the intensity of the band in the UV region (approximately 350 nm) and the growth of a small band in the visible region (approximately 450 nm) corresponding to the $n-\pi^*$ transition of the cis-azobenzene chromophore (Fig. 2). As was found for the initial trans film, the 0° and 90° polarized UV-Vis spectra of the cis enriched film show no significant difference in intensity, indicating that the chromophores are not aligned (see S3, ESI[†]). The trans geometry of the azobenzene repeat units can be regenerated by irradiation of the cis film with visible light. After exposure of the cis film to a white light source for 10 s, the peak in the visible region indicative of the cis chromophore attenuated and the band in the UV region returned, indicating that photoisomerization from the cis to trans geometry occurred. The cycle could be repeated multiple times. Note that the metastable cis chromophores gradually thermally isomerize to the trans geometry at room temperature over a period of approximately 23 hours (see S4, ESI[†]). The inset in Fig. 2 monitors the intensity at 380 nm and 460 nm after repetitive cycles of UV and visible light exposure. Interestingly, the intensity of the band in the UV region increases after the first few cycles and starts to plateau as the number of switching cycles increases, indicating that absorption increases with usage. After 21 repetitive photoisomerization events ending in the trans-azobenzene form of the film, the sample was analysed with linearly polarized light in the 0° and 90° polarization directions. As found for the initial condition after film preparation, the structure of the film shows no alignment (0° and 90° spectra overlap) when photo-switching is performed with light sources that are not polarized.

After demonstrating that the azobenzene chromophores retain their photo-switching capabilities after exposure to green light and polymerization, we investigated the potential for the system to undergo photoalignment in order to understand if the orientation of the azobenzene chromophore in the polymerized film can be controlled with linearly polarized light. The sample that was subjected to multiple cycles of *cis-trans* isomerization (Fig. 1) was first exposed to UV light for 3 s to generate the cis isomer, followed by exposure to polarized blue light for 1 hour to rapidly interconvert between the trans and cis isomers with an anisotropic light source. Analysis of the UV-Vis spectra of the resulting film with light polarized at 0° (parallel) and 90° (perpendicular) shows that the azobenzene-based polymer film undergoes photoalignment when irradiated with polarized blue light as the 0° and 90° polarized spectra show a clear difference in intensity. The spectrum obtained with light polarized at an angle of 0° is markedly more intense than the spectrum obtained with light polarized at 90°. The dichroic ratio, R, is the ratio of absorption at each of these conditions and was calculated using eqn (1) at 342 nm

$$R = \frac{Abs_{0^{\circ}}}{Abs_{90^{\circ}}} \tag{1}$$

to be approximately 2.03, whereas the dichroic ratio in the unexposed region is approximately **1**. These values compare well with

published dichroic ratios for relevant azobenzene-based materials. For example, Ikeda et al. reported values of 1.20-1.41⁵⁵ and White et al.56 reported a value of 1.12 for azobenzene-based oriented liquid crystalline network films. Note that systems consisting of free azobenzene dyes, which are significantly less confined than the crosslinked polymer film in our system, can show much higher dichroic ratios.⁵⁷ The photoaligned area of the substrate shows a clear localized birefringence when rotated between crossed polarizers as shown in Fig. 2 (bottom right). When a fresh sample was made and photoaligned after only one cycle of UV exposure, the dichroic ratio after 1 hour of exposure to polarized blue light was found to be approximately 1.30. The reduced difference between the 0° and 90° spectra when the sample has not undergone multiple photoisomerization events indicates that a burn-in effect enhances the dichroic ratio when the system is repeatedly cycled between cis and trans isomers. Note however that the reduced dichroic ratio value of 1.30 still compares well to published data. When a fresh spot was exposed to polarized blue light for 1 hour without prior exposure to UV light, very little dichroism was observed (dichroic ratio of 1.08) (S5, ESI⁺). When the same spot was then exposed to UV light for 3 s followed by blue light for 1 hour, the dichroic ratio increased to 1.31 (S6, ESI⁺). Collectively, these results indicate that the history of the sample affects the photoalignment capacity. The photoalignment is activated or enhanced by first exposing to UV light and the propensity to photoalign is enhanced by prior photochemical cycling between the cis and trans geometries of the azobenzene repeat units.

When the formulation based on 1 is spin-coated and cured, the film exists in an isotropic structure and shows no dichroism (see S2, ESI[†]). When the cured film is exposed to UV light, the trans isomer photoisomerizes to the cis isomer. This perturbation facilitates photoalignment. When the system is exposed to polarized blue light (445 nm), the azobenzene chromophore rapidly interchanges between the trans and cis geometries as both isomers absorb at 445 nm. The linear trans isomer has a maximum absorption of the polarized light when the transition dipole of the molecule is aligned parallel to the direction of the linearly polarized light, and will show minimum absorption when the transition dipole of the molecule is aligned perpendicular to the polarization direction of the blue light. In transazobenzene, the transition dipole is parallel to the long axis of the rod-like molecule. Each time the molecule undergoes a cycle of trans-cis-trans photoisomerization, the orientation of the trans isomer in the film changes due to molecular level movement caused by the molecular level switching motion. Over an extended irradiation time, all the azobenzene chromophores will tend to align perpendicularly to the linearly polarized electromagnetic field and form a monodomain nematic phase. After photoalignment, the intensity of the UV-Vis bands in the electronic absorption spectrum are dependent on the polarization of the UV and visible light used by the spectrometer in the analysis of the film. Fig. 3 shows how the intensity of the spectroscopic signal at 342 nm for a photoaligned film changes as the polarization angle of the light in the spectrometer is changed. At 0° and 180° , the signal is at maximum intensity. At 90° and 270°, the light in the spectrometer is

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Fig. 3 Polar plot of the peak absorption values at 342 nm (π – π *) for the photoaligned azobenzene polymer film as a function of polarization angle. Polarized UV-Vis spectra at angles ranging from 0–350 degrees were measured for a photopolymerized thin film that was photoaligned by exposure to polarized blue light for 10 minutes (exposed to UV light for 3 s prior to blue light exposure). As the polarization angle of the light in the spectrometer changes, the intensity of the UV-Vis signal at 342 nm changes accordingly. The maximum signal occurs at polarization angles of approximately 0 and 180 degrees. The minimum values occur at polarization angles of approximately 90 and 270 nm.

perpendicular to the alignment direction of the nematic liquid crystalline elastomer and the absorption is at a minimum. As the polarization angle is adjusted in 10 degree increments, the intensity of the signal decreases from 0° to 90° and increases from 90° to 180° . A second minimum is found at 270° (note that light polarized at an angle of 270° is the same as 90°). The anisotropic nature of the change in the spectroscopic signal with polarization angle indicates that the liquid crystalline chromophores are aligned in a monodomain manner. Note that the sample shown in Fig. 3 was irradiated with polarized blue light for 10 minutes after 3 s of irradiation with UV light. The sample was not subjected to continuous cycles of UV and visible light exposure. The dichroic ratio for this sample is approximately 1.18, which is lower than the sample irradiated for 1 hour with blue light (see above). Note that when a film is irradiated with blue polarized light for 10 minutes without prior irradiation with UV light no dichroism is detected (see S7, ESI[†]).

The greatest advantage of the current system is that it combines photolithographic curing, photo-alignment and reversible photo-switching in a single spin-coated film when addressed with multiple wavelengths of light. Four general wavelength regions are employed to realize the full spectrum of film manipulation. Irradiation with green light through a photo-mask generates a cured and patterned film. The molecular structure of the individual azobenzene repeat units in the photopolymerized film can be interchanged between *trans* and *cis* isomers by exposing the material to UV (365 nm LED) and visible light (basic white light source). The patterned regions of the azobenzene polymer film prepared with UV light followed by polarized blue light exhibit selective birefringence in which the *trans*-azobenzene chromophores are aligned in the same direction. Note that no alignment occurs when light sources that are not linearly polarized are used.



Fig. 4 Irradiation of patterned films with UV light followed by polarized blue light results in the formation of a birefringent pattern. Rotating the photoaligned pattern between crossed polarizers shows that the amount of light passing through the sample varies with the angle of the sample relative to the angle of the top and bottom polarizer. The brightest pattern appears when the patterned and photoaligned film is positioned at angles of approximately 45°, 135°, 225° and 315°. For a video of the birefringence, see Video-S1 in the ESI.†

Exploiting the versatile wavelength specific photo-addressability of the material allows for the creation of a birefringent photopatterned film as shown in Fig. 4. Rotation of the film between crossed polarizers shows how the intensity of the light passing through the patterned elastomer changes as the angle of the film with respect to the crossed polarizers changes. For every 45 degrees of rotation of the sample, birefringence of the patterned regions in the polymer film between crossed polarizers appears, indicating monodomain alignment. Irradiation of the system with UV light photo-generates the *cis* isomer which disrupts the liquid crystalline orientation and erases the birefringence. The birefringent pattern can be re-written and erased by exposing to polarized blue light and UV light (S8, ESI†). See S11 (ESI†) for polarized optical microscopy images showing birefringence.

An important aspect of generating a highly efficient birefringent pattern is that the sample must first be irradiated with UV light prior to irradiation with linearly polarized blue light. Photoisomerization to the cis conformation of the azobenzene chromophore possibly improves the mobility of the dye, enhancing its propensity to undergo photoalignment. Additionally, we found that the presence of solvent facilitates photoalignment, which is associated with increased mobility of azobenzenes and LCs. It was observed that drying a drop of azobenzene solution in toluene under a polarized blue laser results in a birefringent spot (S9, ESI⁺). A related and more applicable approach involved placing a drop of toluene on a film cured with green light and exposing to blue polarized light while the toluene evaporated. After ten minutes of exposure to polarized blue light the toluene evaporated and the portion of the film that was exposed to both polarized blue light and toluene exhibited birefringence (S10, ESI[†]). Applying an overlayer of solvent to enhance photo-alignment is somewhat reminiscent of the use of solvent to aid photo-induced bending motions in azobenzene-based polymers.48 The use of UV light rather than solvent is preferred as it is safer, avoids volatile organic compounds (VOCs) and is easier to control.

Conclusions

We have shown that photo-patterning and photo-alignment can be achieved in a single azobenzene-based material by formulating so that the curing and photoalignment processes occur at sufficiently different wavelengths. The material is first cured and patterned with green light. After rinsing away uncured material, the sample is exposed to UV light to photoisomerize the azobenzene chromophores to cis isomers. Irradiation of the cis enriched film with polarized blue light produces a monodomain nematic film exhibiting birefringence and can have a dichroic ratio greater than 2 at 342 nm provided that the sample is photoisomerized multiple times before final alignment. Spin-coated azo-LC thin films can be used as negative photoresists, and the direction of the LC mesogen can be directly controlled by the polarization direction of the exposed polarized light without surface alignment materials. The photoaddressable azobenzene repeat units and the possibility to adjust the absorption properties provides exciting possibilities in applying the material to applications in micro-electromechanical devices as well as novel optical materials.

Conflicts of interest

There are no conflicts to declare.

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