

Supporting Information

Unravelling the photothermal and photomechanical contributions to actuation of azobenzene-doped liquid crystal polymers in air and water

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Experimental description

LCN fabrication procedure:

The liquid crystal polymer network utilized in this study are fabricated through the photopolymerization of liquid crystalline monomers, a diacrylate, (LC mesogen 1, RM82; Merck) and a monoacrylate, (LC mesogen 2, RM 23; Merck) and initiated by a photoinitiator (Irgacure 819, 1mol%, Ciba). The addition of the azobenzene moiety give rise to light responsive behavior. All azobenzene mesogens are commercially available, MR azo is supplied by Sigma Aldrich and MY and DY by SYNTHON Chemicals GmbH. Prior to polymerization, the monomers were dissolved in dichloromethane (DCM) to obtain a homogeneous mixture, subsequently the solvent was evaporated. Polymerization is done in a glass cell, made by gluing two glass slides together with glue containing 20 μm glass bead spacers. Prior to cell fabrication, the independent glass slides were coated with polyimide alignment layers; for a splay alignment one slide contained planar and the other homeotropic alignment layers, Optimizer AL 1051 (JSR Micro) and 5661 polyimide (Sunever), respectively. The cells were filled with the LC mixture through capillary action. Cell filling was done at 95 $^{\circ}\text{C}$, at this temperature the LC mixture is isotropic. The filled cell was then cooled to 80 $^{\circ}\text{C}$, at which temperature the LC mixture is nematic and the 15 minutes-photopolymerization of the mixture was done with an Exfo Omnicure S2000 lamp. A thermal treatment at 120 $^{\circ}\text{C}$ for 10 minutes released thermal stresses arising from polymer shrinkage during polymerization. After polymerization, the cell was opened, and the films are peeled from the glass with razor blades and cut into strips, in which the alignment direction of the planar side is parallel to the long side of the film. The cut strips are 2 cm long and 0.5 cm in width.

Characterization methods:

Thermo-mechanical analysis

Mechanical properties are studied through dynamic mechanical analysis (DMA Q800 from TA instruments); the environmental temperature is measured with a thermocouple. For the determination of storage modulus at different illumination intensities, a high-speed thermal camera (Gobi from Xenics) tracks the film's surface temperature during exposure to one or two light emitting diodes (LEDs) from ThorLabs, emitting at 365 or 455 nm (Figure S9).

Isomerization kinetics

The kinetics of the azobenzene doped LCN films is investigated using a setup installed inside a UV/Vis spectrophotometer (Shimadzu UV-3102). The setup (Figure S10) allows for the absorbance of the films to be measured directly after illumination, minimizing delays between illumination and measurement.

Actuation analysis

The light responsive actuation of the films is investigated in both air and water environments after the films have been stored in the dark. During light actuation, the film unbends towards the light source and the position of the end tip of the film is tracked over time to monitor the degree of actuation with varying incident light intensity. Congruent with the light actuation in dry environment, the film's surface temperature is tracked with a high-speed thermal camera (Figure S11). To ensure that the initial isomer concentrations in the films of longer cis life-times (DY-and MY-azo films) are similar, we perform a pre-illumination step in which the films are illuminated with 455 nm light (250 mW/cm²) for 3 minutes. For in-water actuation (water at 18 °C) we assume an isothermal environment, as any temperature increase of the film during illumination would immediately be lost to the aqueous surrounding. We have tracked the water temperature in the vicinity of the film during illumination and observed a maximum 1-2 °C increase. For in-water actuation analysis we correct for any light absorbed by the water before reaching the sample. We measured that for blue light, 14% of the light is absorbed before reaching the sample and for UV light this is 24%. The pre-bent geometry of the analyzed films differs when comparing the monoacrylate azobenzene containing films with the diacrylate dyes. We observed a less pronounced pre-curl for film containing DY azobenzene. We believe that this may be caused by undesired photoisomerization during polymerization of the films (even though we have utilized a light filter <400nm during polymerization). Unwanted isomerization may have occurred with all azobenzene dyes, yet the crosslinker nature of DY chromophore may lead to a macroscopic manifestation of this undesired isomerization, causing a less pronounced pre-curl.

Absorbed energy calculations

The differing absorbance profiles between azobenzene moieties DY, MY and MR, as well as differing absorption profiles for trans and cis isomers, results in different absorbed energy intensities when the films are irradiated with 365 or 455 nm light. To calculate the effective energy absorbed by each film we have considered the LED spectra of the lights used (Figure S12), as well as the absorption profiles of the LCNs, also considering the trans and cis states absorbance of chromophores MY and DY (Figure S13). By connecting the LED spectra and the absorbance of the films we conclude that: MR films absorb 83% of the incident 455 nm light; MY and DY films with a dominant cis population absorb 60% of 365 nm light (and 53% of 45 nm light); MY or DY films with a dominant trans population absorb 50% of 455 nm light (and 88% of 365 nm light). We have shown that isomerization is a rapid process (see Figure S8), hence for simplification we consider the cis state spectra for absorbed energy calculations considering 365 nm illumination and trans state absorbance spectra 455 nm illumination (for MY and DY films).

Table 1 Chemical compositions of the mixtures used

	Mixture MY	Mixture DY	Mixture MR
LC mesogen 1	56,5 mol%	54,5 mol%	56,5 mol%
LC mesogen 2	40,5 mol%	42,5 mol%	40,5 mol%
MY - azo	2 mol%		
DY - azo		2 mol%	
MR - azo			2 mol%
IRGACURE 819	1 mol%	1 mol%	1 mol%

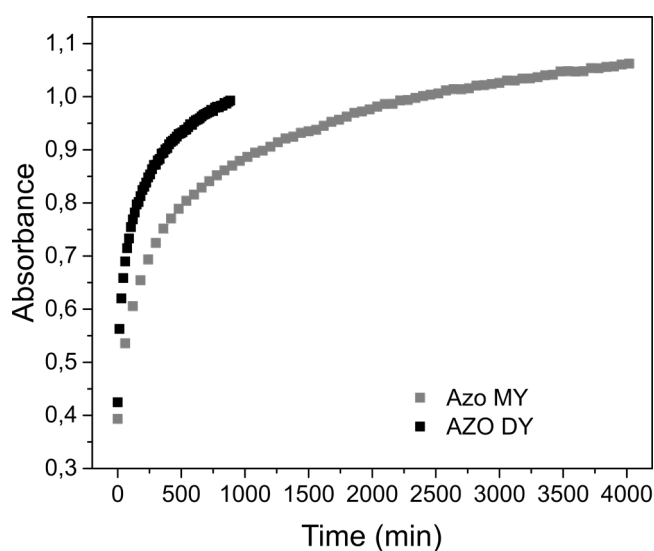


Figure S1. Evolution of the 365 nm absorbance peak of an LCN doped with either DY or MY after 3 min exposure to 365 nm light. This plot shows the cis-trans isomerization over time.

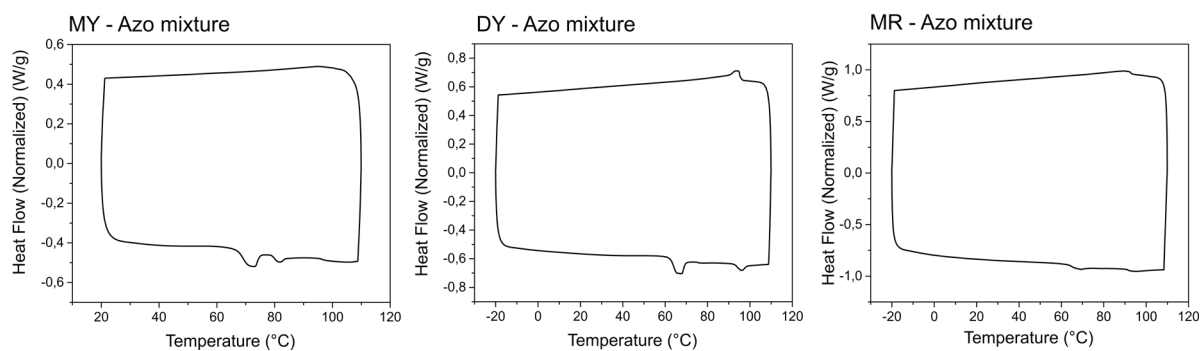


Figure S2. Differential scanning calorimetry scans (second runs) of the LC mixtures used in the study (Figure 1B, C).

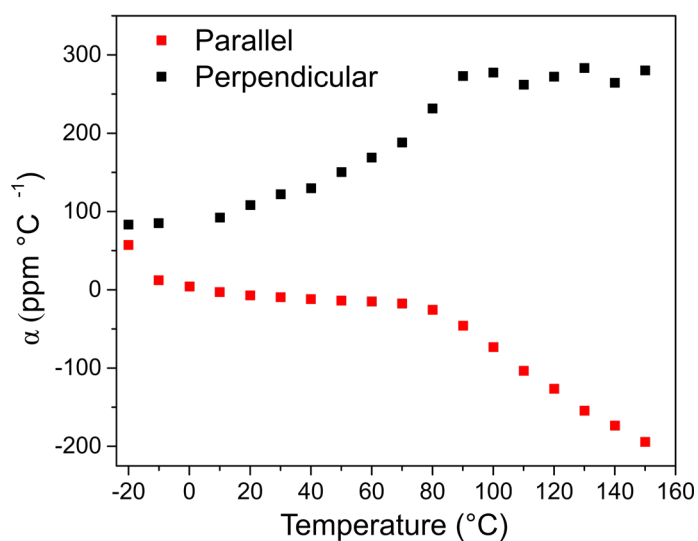


Figure S3. Coefficients of thermal expansion of the LC network (Figure 1B), red squares and black squares show CTE parallel and perpendicular to the molecular long axis, respectively. Reference temperature is taken to be -20 °C.

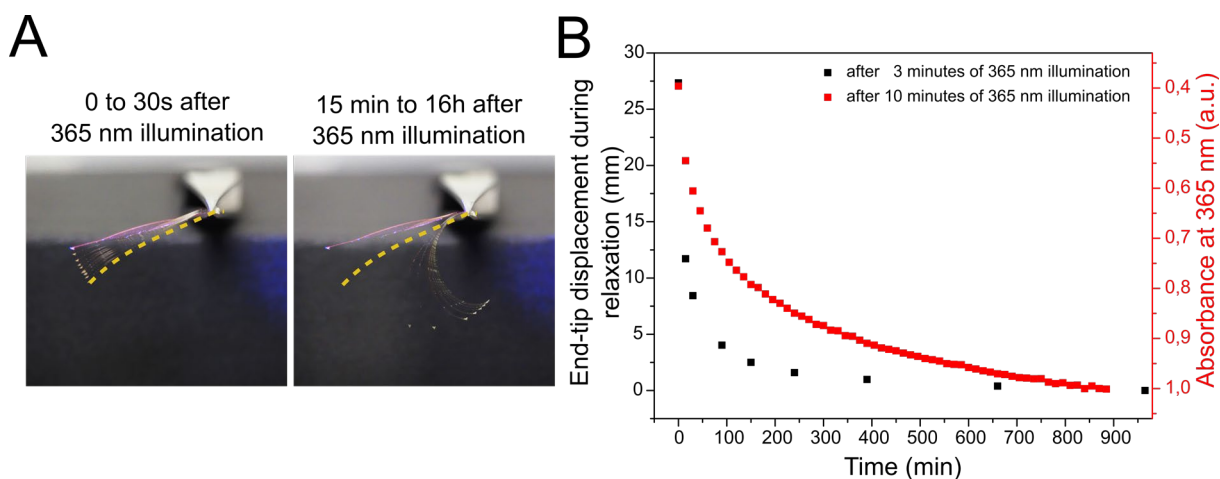


Figure S4. Timescale mismatch between isomerization kinetics (*trans* isomer population recovery) and the macroscopic return to the pre-curved shape of the LCN film (DY azo) after 365 nm illumination in dry environment. **A.** Macroscopic recovery of the pre-curved film before illumination with 365 nm. The first image stack shows the deformation recovery after 30s after 365 nm illumination is removed. The second stack shows the recovery between 15 min up to 16h. **B.** Plot displaying the displacement recovery and the recovery of the 365 nm peak, corresponding to the *trans* azobenzene isomer absorption.

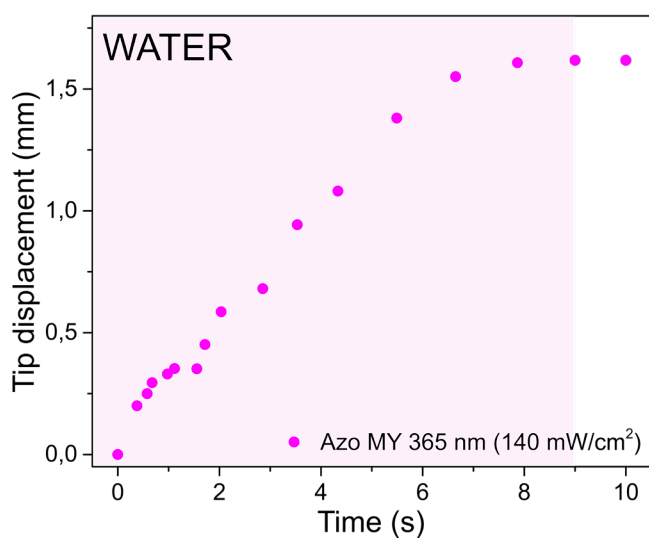


Figure S5. End tip displacement of an LCN film containing MY azo when illuminated by 365 nm light under water. The deformation is minimal and reverse actuation is possible through exposure to 455 nm light.

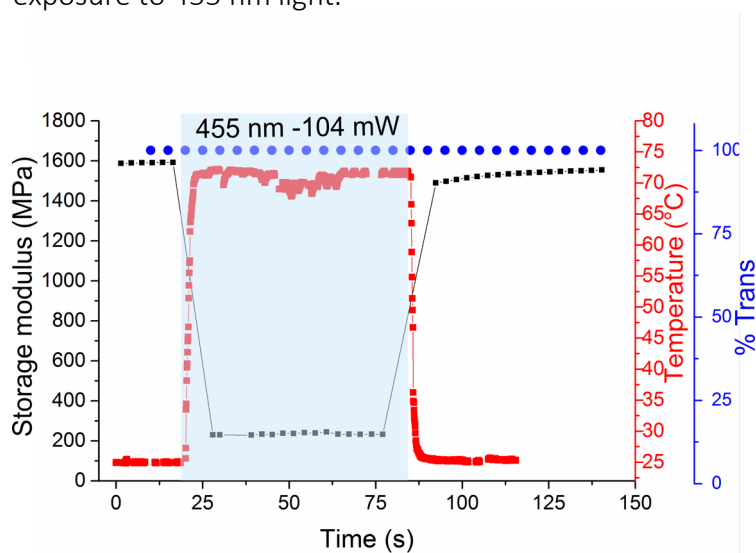


Figure S6. Overlay of changes in isomer population, film temperature and storage modulus during illumination of a splay aligned LCN doped with azobenzene derivative MR.

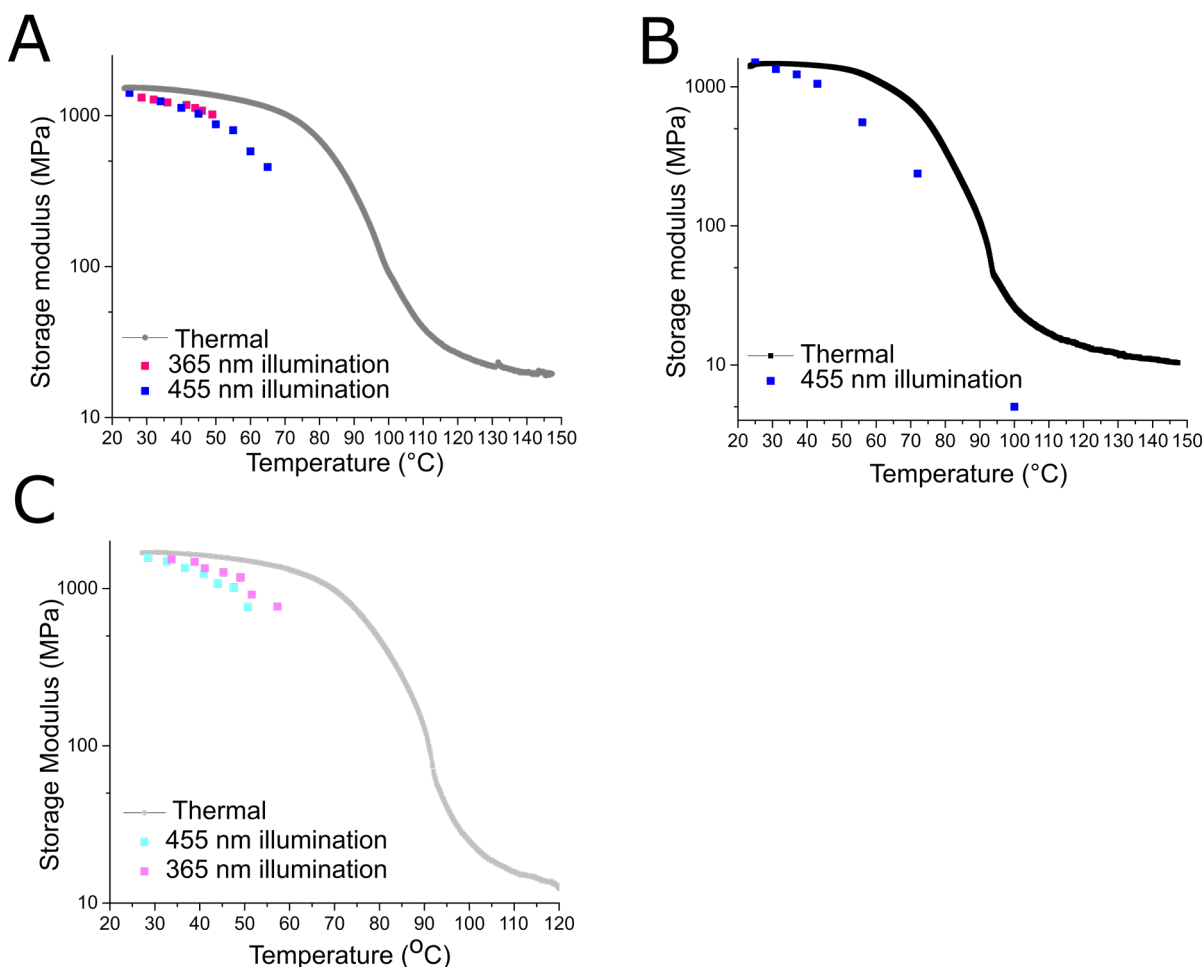


Figure S7. Comparison between thermal-softening and photo-softening of the polymer networks. Thermal-softening caused by temperature increase in DMA oven. Photo-softening caused by heating through sample illumination either 365 or 455 nm light. A. Film containing MY azo. B. Film containing MR azo. C. Film containing DY azo.

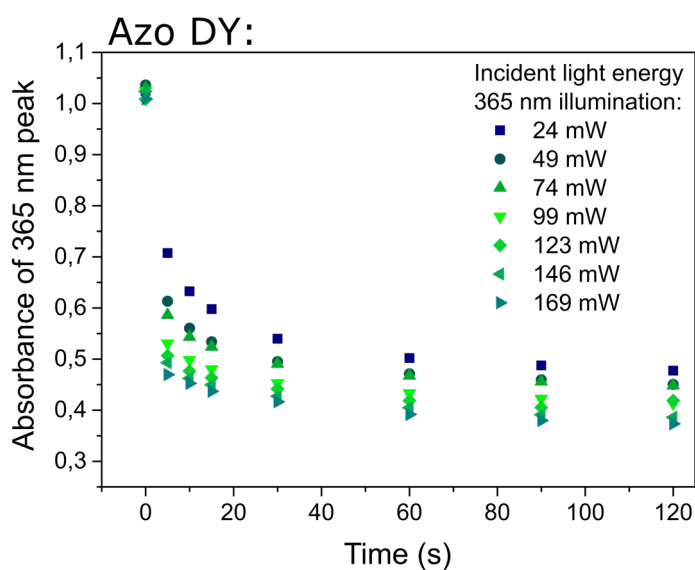


Figure S8. Evolution of 365 nm absorbance peak for film doped with azo-DY upon exposure to 365 nm light of different energy intensities. High trans-cis conversions are already attained at low incident light energies.

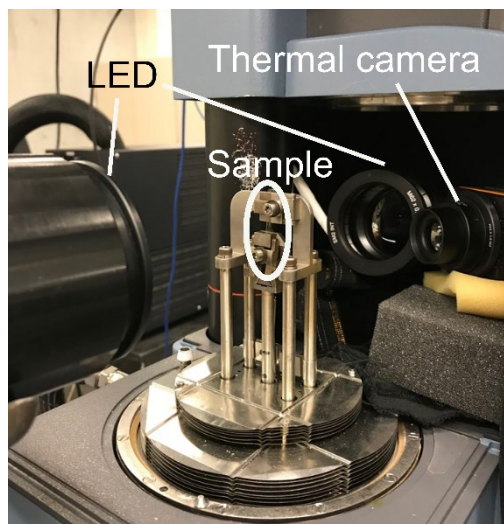


Figure S9. Setup for the dynamic mechanical analysis of the polymer films upon illumination. The setup contains the LEDs and a high-speed thermal camera to record the surface temperature of the film. Temperature tracking is done with a high-speed infrared camera (Gobi, Xenics).

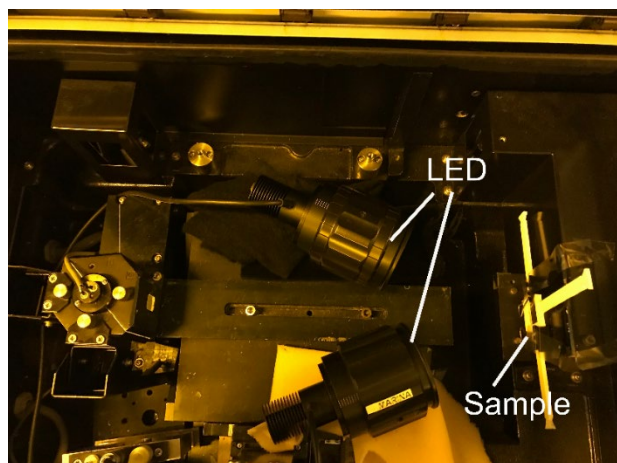


Figure S10. Setup for the isomerization kinetics study. The setup allows for illumination of the sample inside the spectrophotometer, minimizing delay between illumination and measurement.

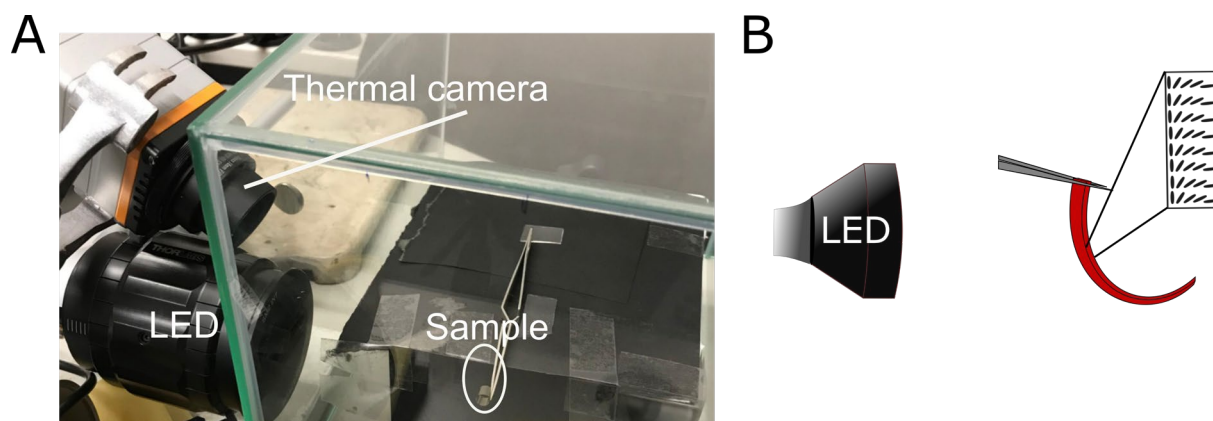


Figure S11. A. Setup for analysis of the actuation of the polymer films upon illumination. The setup contains the LEDs and a high-speed thermal camera to record the film's surface temperature. The actuation videos are taken with the film inside a glass box, to avoid disturbances from air currents. Before actuation, the lights in the room are switched off. The sharp focus of the LED is approximately 1 cm². **B.** Schematic depiction of the LCN position and LED orientation during actuation.

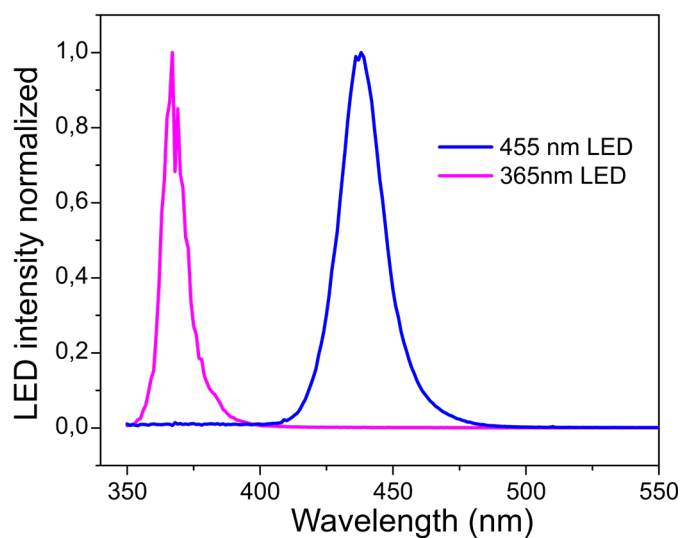


Figure S12. Normalized intensity spectra of the LEDs used for all the actuation analysis.

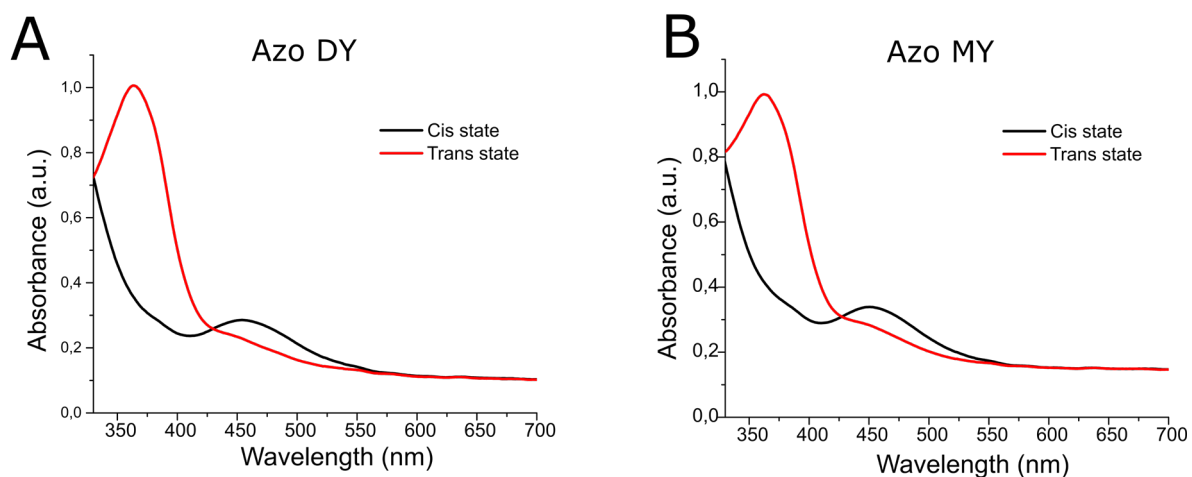


Figure S13. UV-VIS spectra of *cis* and *trans* states of splay films containing DY (A) or MY (B) azobenzene derivatives. The *cis* state spectrum is obtained after illumination of the films with 365 nm light of 170 mW/cm² for 3 minutes and *trans* spectra correspond to the isomer population after 3 min illumination of 455 nm of 320 mW/cm².