

A high frequency photodriven polymer oscillator†

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High frequency and large amplitude oscillations are driven by laser exposure in cantilevers made from a photosensitive liquid crystal polymer.

Synthetic materials that imitate natural motion are one of the inspirations behind the development of stimuli-responsive polymers, namely self-tying shape-memory sutures,¹ micromechanical devices,² electro-active polymer (EAP) muscles,³ or liquid crystal polymer networks (LCNs).⁴ LCNs are particularly interesting as the inherent anisotropy in the polymer network amplifies the mechanical properties and can serve as a trigger for reversible mechanical deformations through order parameter reduction or reorientation of the polymer network. The introduction of photoisomerizable azobenzene molecules into LCNs yields materials where light input can be converted into mechanical output.^{5–9} We report on the photodriven, fast (~ 30 Hz), and large amplitude ($>170^\circ$) oscillation of a polymer cantilever consisting of a monodomain azobenzene-containing LCN (azo-LCN). The frequency of the photodriven oscillation is similar to a hummingbird wingbeat, which can range from 20–80 Hz.¹⁰ The oscillation of the azo-LCN cantilever can be turned on and off by switching the polarization direction of the driving laser beam, and the behaviour shows little fatigue over 250 000 cycles. With engineering and miniaturized designs, photodriven oscillations of azo-LCN materials could be an enabling technology for photo-fueled miniature flying machines, remotely controlled micro-optomechanical systems, or light-controlled microfluidic valves.

The mechanism for the photoresponse of azo-LCNs is determined by the wavelength of the radiation source. UV radiation (365 nm) efficiently isomerizes the azobenzene linkage from *trans* to *cis*. The generation of *cis*-azobenzene in LCNs induces a mechanical response through a relative volume change from a reduction of (a) the order parameter of the network and (b) the molecular length of the azobenzene unit from 9 Å to 5.5 Å.¹¹ If the UV light is linearly polarized, the azo-LCN will contract parallel to the polarization

direction.⁹ Polarized radiation with wavelengths in the 440–515 nm region of the visible spectrum, where both *trans* and *cis* isomers have comparable absorption, results in realignment of molecules perpendicular to the polarization direction.^{12–14} The reorientation of the azobenzene mesogens is accommodated by the polymer network, which contracts along the direction of the polarization and expands orthogonal to the polarization direction. Realignment of azobenzene mesogens with 442 nm, 488 nm, or 514 nm laser light is extensively utilized in the formation of surface relief gratings in azobenzene polymers¹⁵ and referred to as *trans-cis-trans* reorientation. Photoactuation of azo-LCNs with light in the range of 440–515 nm can be advantageous as *trans-cis-trans* reorientation is rapid and effective at temperatures below the glass transition (T_g) of the polymer.¹⁶ In polydomain azo-LCNs, reorientation of azobenzene mesogens drives bidirectional photoactuation of $\pm 70^\circ$ controlled by laser beam polarization.¹⁶

The azo-LCNs detailed here were prepared by the thermal copolymerization of two azobenzene liquid crystal monomers, in the aligned nematic phase.^{9,16} Wide-angle X-ray diffraction confirms the LCN is monodomain. Further detail regarding the synthesis of the azo-LCN studied here is included in the ESI.† Photoactuation is driven with a simple optical setup consisting of an argon-ion laser (Ar^+), a polarization rotator, and a spherical lens (Fig. 1). The Ar^+ laser beam is multiwavelength, containing 457 nm, 488 nm, and 514 nm light and capable of driving both *trans-cis* and *cis-trans* isomerization. Fig. 1b presents still images that illustrate the response of the monodomain azo-LCN cantilever to the polarized laser beam. As seen in Fig. 1b-i (frontal view), the nematic director is parallel to the long axis of the polymer cantilever (dimensions 5 mm \times 1 mm \times 50 μm). Upon exposure to a 0.3 W cm^{-2} Ar^+ laser beam polarized orthogonal to the nematic director of the polymer ($E \perp n$), the tip of the cantilever is displaced nearly 40° towards the source (Fig. 1b-ii). Subsequent rotation of the polarization parallel to the original nematic director of the polymer ($E \parallel n$) increases the tip displacement to nearly 90° (Fig. 1b-iii). If the laser beam is blocked while the cantilever is in either position, the cantilever returns to its original position (Fig. 1b-iv, side view), likely due to elastic recovery of unexposed regions and entropic restoring forces imparted by the network within the exposed region, rapidly reorienting the photo-driven mesogens to realign to the global monodomain. Unlike polydomain azo-LCNs,¹⁶ monodomain azo-LCNs deflect in only one direction.

Increasing the intensity of the laser beam to 0.8 W cm^{-2} causes the cantilever to oscillate at a frequency of nearly 30 Hz (Fig. 2, video 1†). Images of the oscillating azo-LCN cantilever are shown in Fig. 2a-i (full color) and Fig. 2a-ii (540 nm cut-off filter) and the oscillation cycle is shown in Fig. 2b. In Fig. 2a, the displacement angle between the two extremes is greater than 170° . The distance travelled by the tip

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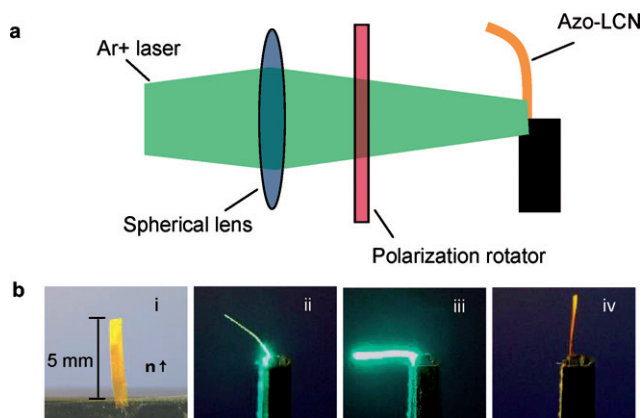


Fig. 1 (a) The azo-LCN cantilever is photoactuated in a simple optical setup utilizing the multiwavelength output (457, 488, 514 nm) of an argon-ion (Ar^+) laser, a spherical lens, and a polarization rotator. (b) The azo-LCN cantilever is positioned with the nematic director (n) parallel to the long axis of the polymer of dimension $5 \text{ mm} \times 1 \text{ mm} \times 50 \mu\text{m}$ (i, frontal view). When exposed to 0.3 W cm^{-2} of light polarized orthogonal to n ($E \perp n$), the cantilever bends from vertical (i) to 42° towards the laser source (ii). The azo-LCN cantilever bends to almost 90° (iii) with exposure to the Ar^+ laser beam polarized parallel to n ($E \parallel n$) from either the orthogonally polarized state (ii) or the unexposed state (i). If the laser is blocked at any point, the cantilever returns to its original position (iv).

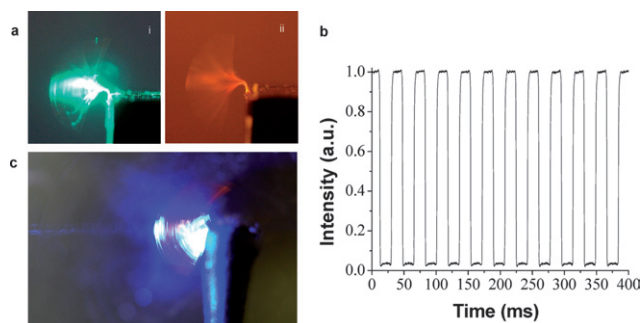


Fig. 2 (a) Oscillation of an azo-LCN cantilever upon exposure to a 0.8 W cm^{-2} Ar^+ laser beam (i—color, ii—laser light filtered). The amplitude of the oscillation is greater than 170° . (b) The frequency of the oscillating azo-LCN cantilever was measured optically and determined to be 28.4 Hz . (c) The oscillation can also be driven with similar intensity from a He–Cd (442 nm) laser beam.

of the cantilever during a half-cycle is approximately 7 mm at an average velocity of nearly 200 mm s^{-1} ($4.8^\circ \text{ ms}^{-1}$). Previous observations of photomechanical deformation in LCN systems have been exclusively non-oscillatory in nature and more than an order of magnitude slower.

The photodriven oscillation of monodomain azo-LCN cantilevers depends on the laser wavelength, laser intensity, cantilever thickness, cantilever aspect ratio, and azo-LCN domain structure. Oscillations are driven with similar intensity of monochromatic 442 nm light from a He–Cd laser (Fig. 2c) but are not observed under exposure to laser light of 532 nm . As shown in Fig. 3, the amplitude of the oscillating azo-LCN cantilever can be regulated with laser intensity. Above a threshold energy requirement, increasing laser intensity increases the amplitude of the oscillation from very small ($<10^\circ$) to very large

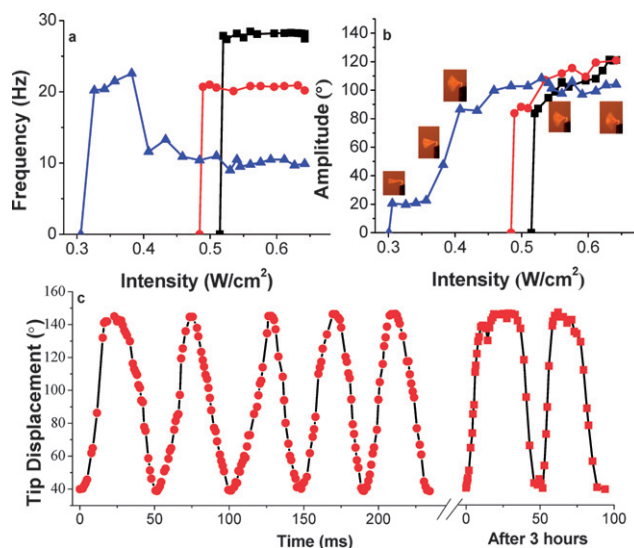


Fig. 3 (a) Frequency and (b) amplitude as a function of intensity for azo-LCNs ($5 \text{ mm} \times 1 \text{ mm}$) with $50 \mu\text{m}$ (■), $40 \mu\text{m}$ (●), and $20 \mu\text{m}$ (▲) thickness. (c) The oscillation of the azo-LCN cantilever ($5 \text{ mm} \times 1 \text{ mm} \times 50 \mu\text{m}$) is represented in a plot of tip displacement angle against time. With exposure to a 0.56 W cm^{-2} beam from an Ar^+ laser, the cantilever oscillates from 40° to approximately 150° at a frequency of 23.1 Hz . After three hours of continuous exposure, the cantilever continues to oscillate at 22.2 Hz .

(170°). The laser intensity threshold to drive azo-LCN cantilever oscillation and the corresponding frequency depends on cantilever thickness (Fig. 3b). For example, increasing the thickness of the azo-LCN from $20 \mu\text{m}$ to $50 \mu\text{m}$ increases the laser intensity threshold for photodriven oscillation from 0.3 W cm^{-2} to 0.45 W cm^{-2} while also increasing the oscillation frequency from 10 Hz to nearly 30 Hz . To enable photodriven oscillation, the monodomain azo-LCN cantilever must have dimensions such that the length is greater than the width. The best performance occurs when the nematic director is parallel to the long axis of the cantilever. Notably, photodriven oscillations of polydomain azo-LCNs were not observed. The oscillation can be driven for long time periods without significant fatigue. As seen in Fig. 3c, with a driving intensity of 0.56 W cm^{-2} (amplitude 110°), the oscillation frequency decreases only slightly from 23 to 22.3 Hz after three hours of continuous operation (250 000 cycles). Additional fatigue beyond three hours is not observed for up to eight hours of continuous operation.

The oscillation of the azo-LCN is illustrated in Fig. 4 and the mechanism is described hereafter. Succinctly, the effect is enabled by the time scale of the photoisomerization of azobenzene, the restoring force of monodomain LCN, bimorph cantilever dynamics, and their resulting impact on physical quantities during mechanical displacement, particularly the moment of inertia. Increasing the intensity of the laser beam increases the displacement angle in azo-LCN systems. Therefore, increasing the laser intensity from 0.3 W cm^{-2} (Fig. 1) to 0.8 W cm^{-2} (Fig. 2) increases the moment of inertia for the azo-LCN cantilever above a threshold that enables the cantilever to deflect through the path of the laser beam, so that the back surface of the azo-LCN is exposed to light. The azobenzene molecules at the back surface of the polymer, which due to attenuation of light in the polymer film are not exposed to an appreciable amount of light from the Ar^+ source, subsequently undergo photoisomerization. The

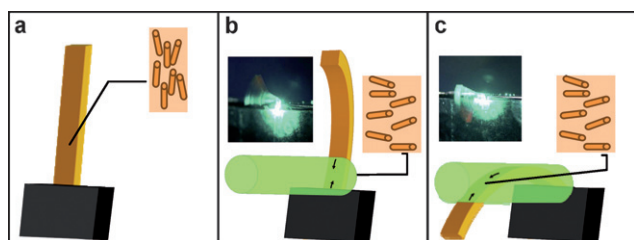


Fig. 4 The mechanism of the azo-LCN cantilever oscillation is illustrated. (a) Initially, the azobenzene mesogens are aligned vertically. (b) The front surface of the cantilever is exposed during the upstroke and (c) the back surface is exposed during the downstroke. During the oscillation, the azobenzene mesogens on the illuminated surface of the azo-LCN reorient due to a statistical buildup of *trans*-azobenzene orthogonal to the polarization direction of the laser beam.

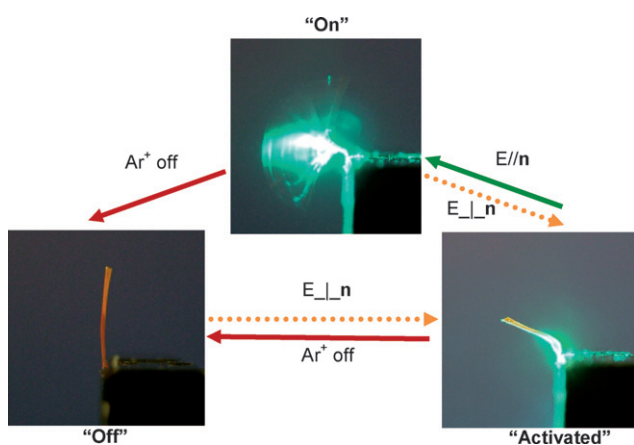


Fig. 5 The optical protocol for turning the azo-LCN cantilever oscillation “on” and “off”. Cycling the Ar⁺ laser from $E_{\perp n}$ to $E_{\parallel n}$ can turn oscillation “on”. The oscillation is turned “off” by either blocking the Ar⁺ or returning the polarization of the laser beam to $E_{\perp n}$.

contraction now occurring on the back surface of the azo-LCN reverses the displacement direction. As the tip of the azo-LCN again passes through the Ar⁺ beam during the upstroke of the cycle, the front surface is re-exposed. Due to the inherent network structure of monodomain LCNs (e.g. restoring forces previously discussed in Fig. 1b-iv) coupled with the fast dynamics of azobenzene photoisomerization, the front surface assumes its original form with a high concentration of *trans*-azobenzene mesogens aligned along the nematic director of the polymer within the half-cycle of the oscillation (i.e. when it is unexposed). Therefore, the deformation of the azo-LCN caused by contraction on the back surface is halted, and the cantilever again deflects downward to a large angle.

The polarization controlled (Fig. 1b-ii, 1b-iii) angular displacement of the monodomain azo-LCN can be used as an all-optical on/off switch for photodriven oscillation. Fig. 5 summarizes the all-optical cycle (see also video 2†). In the design presented here, exposing the azo-LCN to Ar⁺ with $E_{\perp n}$ “activates” the polymer for oscillation, by

displacing the cantilever towards the laser. Subsequently switching the Ar⁺ polarization to $E_{\parallel n}$ turns the photodriven oscillation “on”. The oscillation can be returned to the “activated” state by returning the polarization to $E_{\perp n}$ or to the “off” state by blocking the laser beam. Only at a laser intensity greater than 0.8 W cm^{-2} does exposure to Ar⁺ laser light with $E_{\perp n}$ induce oscillation, as lower intensity exposure does not input enough energy to deflect the tip of the cantilever through the driving laser beam.

This work demonstrates the potential afforded by a marriage between cantilever mechanics and photodriven, spatially confined changes in LC domains. From a perspective of energy generation in miniaturized materials, photodriven oscillation of azo-LCN cantilevers offer some advantages. Foremost of these, photodriven oscillation of azo-LCN cantilevers are a single monolith containing the force generating unit (i.e. azobenzene mesogens) in a kinematic structure that amplifies motion or transmits work. As such, micro-optomechanical systems could be powered by the high frequency, large amplitude oscillation in a single unit made up of a polymeric material, further simplifying the design of such a system while simultaneously reducing the space and weight requirements. Experimental determination of the photomechanical conversion efficiency of the system is ongoing, but is projected to be in the range of 1–10%.

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