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A four-blade light-driven plastic mill based on hydrazone liquid-crystal networks[☆]



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ABSTRACT

The first light-driven plastic mill is developed, which converts the incoming light directly into a continuous rotation. This device is composed of four blades made of hydrazone-based liquid crystal polymer films able to bend under focused light irradiation and to create a force causing the rotation of the mill. The mechanism of motion originates from the fast photo-thermal isomerization around the C=N bond of hydrazones. We show that by accelerating the rate of the thermal Z to E back-isomerization of hydrazones, macroscopic deformation with fast strain rate can be obtained. The rapid motion of the film is the key factor in obtaining the continuous rotatory motion of the mill. These results broaden the range of molecular switches available for macroscopic motion of light-driven organic devices and offer new insights for single-step energy conversion in soft robotics and automated systems.

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Polymeric stimuli-responsive materials are well-known to adapt their geometries and properties to external stimuli¹ (light, temperature, pH, chemical effectors, etc) and are of great interest to a large variety of applications ranging from drug delivery to actuators and from tissue engineering to advanced coatings. In most cases, these materials oscillate between two (or more) kinetically stable states that interconvert upon the action of an external stimulus. Conversely, self-oscillating materials require the same continuous stimulus to switch back-and-forth from one state to the other in a controlled fashion.^{2–5} Liquid crystal network (LCN) is a class of materials recently employed to create films with triggered macroscopic deformation and self-sustained oscillation.^{6–10} Their inherent anisotropy amplifies the collective molecular motion of switches incorporated within the network.¹¹ Azobenzene is often preferentially chosen as the photo-switch because of its reversible and controlled photo-isomerization.^{5–9,12} When incorporated in a LCN, the geometrical molecular deformation of the azobenzene molecule upon trans to cis isomerization by UV irradiation is translated to the macroscopic level. The cis to trans back-isomerization is induced by illumination with visible light or by

an increase of temperature. When the irradiation of both the trans and cis isomers is conducted simultaneously, but separated in space, the contraction and expansion of a LCN-belt lead successfully to a plastic motor that converts light energy into a rotational movement.⁶

Over the last decades, the diversity of photo-switches used in responsive materials has not been enlarged significantly and those used routinely remain azobenzenes,^{5–9,12} alkenes,¹³ diarylethenes,¹⁴ and spiropyran,¹⁵ each showing their advantages and limitations. Recently, interest has been growing on the use of imines, acylhydrazones and hydrazones as switches¹⁶ due to their multi-adaptive properties. These molecules exhibit a E–Z photo-isomerization around the C=N double bond.¹⁷ The Z to E back-isomerization is induced by heat or light and can be tuned by the constituents present at the periphery of the bond.

Herein, we demonstrate the development of copolymerizable hydrazones as photo-switches in LCN to obtain equilibrium and steady out-of-equilibrium motion at the macroscopic scale: from simple bending/unbending of a polymeric film to self-sustained rotational motion induced by continuous monochromatic light irradiation. We designed, prepared, and studied several hydrazone candidates and we present here the use of two of them, hydrazones **1** and **2**, incorporated in a LCN, to control the bending and the oscillatory motion of the film by light. We link the fast deformation observed to the rate of Z to E thermal back-isomerization of the hydrazones. These results prompted us to investigate the

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engineering of a four-blade light-mill device that can convert the incoming focused light directly into a continuous rotation. The idea is to use the LCN actuators as blades able to bend and unbend rapidly under light irradiation to create a force causing the rotation of the mill. The prerequisite to obtain the continuous motion is to get fast responses of the LCN-blades, which is obtained by the incorporation of hydrazone with a fast thermal relaxation. This sophisticated motion requires the fine tuning of the photochemistry of a switch and the appropriate properties and dimensions of the LCN film to achieve optimized dynamics.

The hydrazones **1** and **2** studied were synthesized in high yield by direct condensation of an aldehyde with the corresponding phenyl hydrazine. The aldehyde unit was chosen such that the hydrazone has a rod-like shape and can align nicely with the LC mixture. The hydrazone compounds precipitated from the ethanol solution as pure E isomers. Conversion from the E to the Z configuration was obtained by light irradiation (Fig. 1). At the molecular scale, light irradiation induces the excitation of the E isomer which then undergoes an out-of-the-plane rotation around the C=N bond to yield the Z isomer.^{17a} The Z to E back-isomerization reaction can be induced by light or heat, following an out-of-the-plane rotation or a nitrogen inversion mechanism.

We prepared LCN films by the photo-polymerization of a mixture of LC acrylate monomers RM82 (65 wt%) and RM23 (30 wt%), hydrazone acrylate **1** or **2** (5 wt%) using a phosphine oxide photo-initiator (<1wt%). The ratio of monoacrylate (RM23) and diacrylate (RM82) monomers in the mixture was chosen such to achieve good processing properties in the monomeric state combined with the required mechanical properties in the polymeric state.¹¹ The hydrazone photo-switches exhibit LC behavior on their own and their long axes comply with the director of other LC monomers. To enhance the macroscopic deformation, the monomer mixture was aligned and polymerized in a splayed configuration over the cross-section of 20 μm .¹⁸ Under light exposure, the anisotropic deformation leads to an expansion at the homeotropic side and a contraction along the long axis of the sample at the planar side inducing larger deformations than planar uniaxial configurations. After polymerization, a glassy and transparent thin film was obtained ($T_g = 48\text{ }^\circ\text{C}$, Figs. S1–S2) and cut in bands of about 2.5 cm long and 0.4 cm width with the director of the planar alignment along the length of the sample. Before analyzing the macroscopic deformation, we studied the molecular relaxations to

arrive at the optimal conditions.

The E/Z isomerization of **1** and **2** embedded in the films was followed by UV/Vis spectroscopy (Fig. 2). Before irradiation, the films **1**-LCN and **2**-LCN exhibited a maximum absorption at 350 nm and 388 nm, corresponding to the **1**-E and **2**-E isomers, respectively. Irradiation of **1**-E-LCN during 5 min at 365 nm showed a decrease of the 350 nm band corresponding to its conversion into **1**-Z-LCN to arrive at its photo-stationary state. The recovery of the isomer **1**-E by thermal relaxation was followed over time at 25 $^\circ\text{C}$ (Fig. 2B). The data obtained fitted well to a stretched first-order kinetics attributed to constraints of the polymer network in its glassy state¹⁹ with the relaxation time of the Z isomer being more than 3 h in the LCN (see S1). The back-isomerization **1**-Z to **1**-E was however accelerated by irradiation at 405 nm or by heating. Overall, the hydrazone **1**-E has the advantage of not absorbing in the visible region and is thus a good candidate for colorless actuators. Next, the irradiation of the film **2**-LCN during 5 min at 405 nm showed a decrease of the 388 nm band and a fast **2**-Z to **2**-E thermal relaxation due to the withdrawal effect of the two nitro groups on the phenyl ring (Fig. 2C). Also here the data obtained fitted to a stretched first-order kinetics with now a relaxation time of the **2**-Z isomer being about 4 min in the LCN.

The macroscopic deformation of the sample **1**-LCN upon light irradiation was first studied. One side of the film was clamped leaving 1.7 cm free to move. The film was curved in the resting state ($t = 0\text{ s}$ in Fig. 3) due to residual stress originating from the polymerization at elevated temperature and subsequent cooling to room temperature. The thermal expansions at both sides of the film have an opposite sign at elevated temperature causing the bending. When the film was irradiated with 365 nm focused LED light, it straightened towards the flat state – i.e. the state at the polymerization temperature – precisely and solely at the position of the focus point of the light (Fig. 3). Within 0.4 s, a large macroscopic deformation was already visible, and the direction of bending or unbending was independent on the side of irradiation.¹⁸ The motion is explained by the reduction of the molecular LC order of the aligned LCN due to the **1**-E to **1**-Z isomerization upon irradiation. The disorder leads to an anisotropic contraction along the molecular director axis and expansion perpendicular to the director axis, placing the planar alignment at the inner side (contraction) and the homeotropic at the outer side (expansion) of the actuated film. According to Beer's law, the absorption coefficient of **1**-LCN is

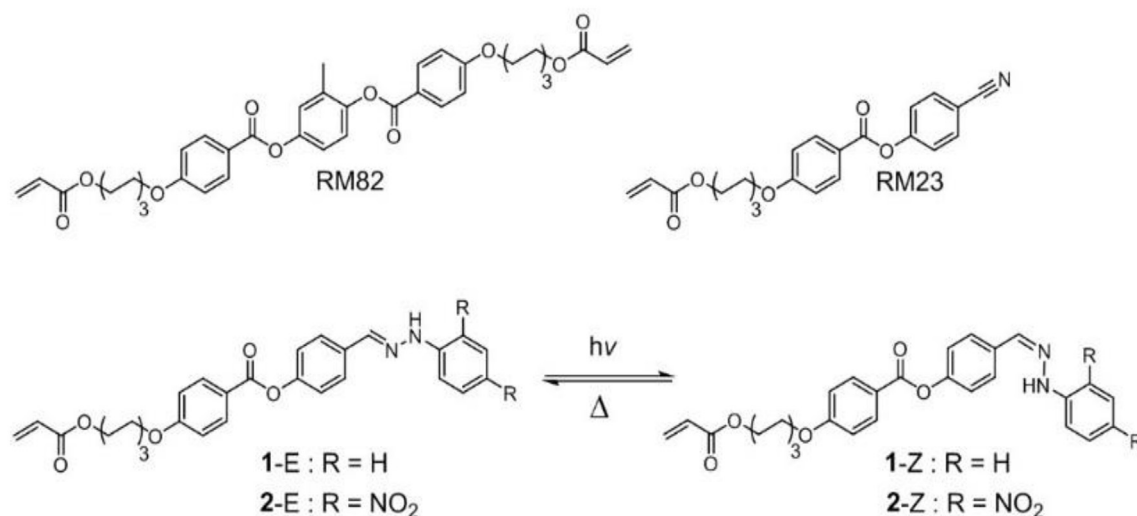


Fig. 1. Mesogens structures and E/Z isomerization of hydrazones **1** and **2**.

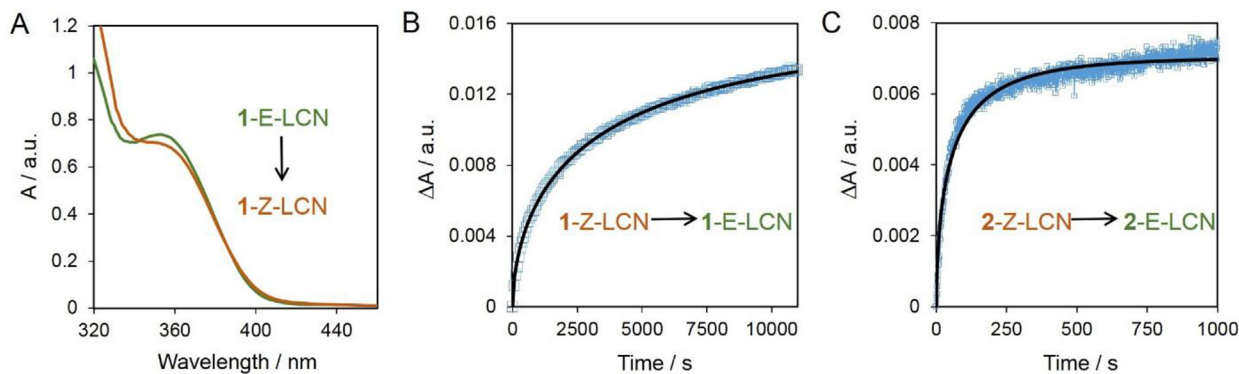


Fig. 2. A) UV/Vis absorption spectra upon photo-isomerization of **1**-LCN (5 μm thick) attached to a glass substrate. Conversion of **1**-E-LCN (green trace) into **1**-Z-LCN (orange trace) at 25 $^{\circ}\text{C}$ over 5 min, 365 nm LED irradiation. B) Difference in absorbance during the back-conversion of **1**-Z-LCN into **1**-E-LCN (blue trace) followed over time at 350 nm, 25 $^{\circ}\text{C}$ and the stretched exponential fit (black trace, see Fig. S3). C) Difference in absorbance during the back-conversion of **2**-Z-LCN into **2**-E-LCN (blue trace) followed over time at 388 nm, 25 $^{\circ}\text{C}$ and the stretched exponential fit (black trace, see Fig. S4).

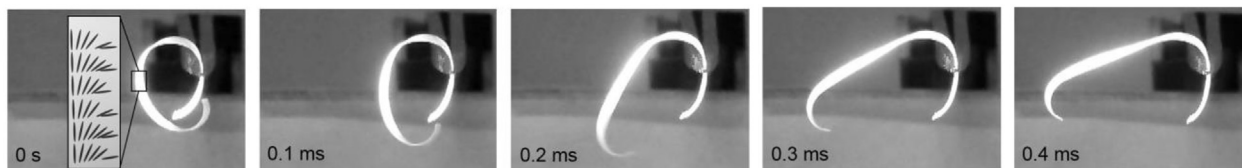


Fig. 3. A sequence of frames over irradiation time showing unbending of the film **1**-LCN by focused light irradiation (365 nm, 0.50 W cm^{-2}). The sample is irradiated from the left, at the planar side. The film straightens at the position of the focus point of the light (where the light intensity is higher) while the most left side of the film irradiated with lower light intensity stays bent. The film geometry is 2.5 cm (length) \times 0.4 cm (width) \times 20 μm (thickness). The inset in the first frame shows the splay alignment.

approximately 330 cm^{-1} at 365 nm, which corresponds to a penetration depth of the light at this wavelength of about 30 μm . It confirms that light actuates the both sides of the 20 μm thin sample by the excitation of the switches through the entire film thickness. When the irradiation was stopped, the film bends back within a second (Fig. S5). However, based on the spectroscopic data of thermal relaxation at room temperature, the full recovery is expected to be obtained in minutes. It was also observed that temperatures up to 60 $^{\circ}\text{C}$ are registered at the hinge of the film upon irradiation (Fig. S6) while the rest of the film stays at room temperature. Moreover, experimental and theoretical studies on sub-molecular effective temperature during irradiation have shown that in the close proximity of photo-switches, temperatures above 200 $^{\circ}\text{C}$ can be reached.²⁰ At high temperatures, the thermal Z to E relaxation rate of hydrazones is increased^{17a,b} and explains the fast relaxation of the film.

Then, the deformation of the film **2**-LCN containing the fast relaxing hydrazone **2** was examined. When the film **2**-LCN was clamped at one end and irradiated with 405 nm LED light, it straightened in the same manner as **1**-LCN but hundredth of seconds faster (the maximum strain was reached in about 0.13 s). And after few seconds in front of the light beam, mechanical oscillations similar to the ones previously reported were observed (Fig. 4, see SI for more details).^{7,10} The period of these oscillations is 80 ms, which also confirms the high speed of displacement of **2**-LCN. Upon removal of the illumination, the film relaxed to its resting state in about 0.4 s. The main difference in the motion of **2**-LCN compared to **1**-LCN or similar LCN doped with azobenzene having stable cis isomer¹⁸ is the fast strain rate obtained at similar light intensities. The mechanism of the fast motion observed originates from the fast cyclic Z-E-Z isomerization around the C=N of **2** due to the fast relaxation of the isomer **2**-Z (Fig. 2) and the increase of temperature

(Fig. S6). During the oscillating motion, the hinge of the film is successively in the light and in the dark due to the self-shadowing by its tip. When the hinge is in the light, the continuous Z-E-Z isomerization of the switch and the increase of temperature induce the bending of the film until its tip shadows its hinge. While the hinge is in the dark, the fast thermal relaxation of the switch and the decrease of temperature induce the unbending of the film until the light reaches the hinge again. The repetition of this sequence gives rise to the continuous oscillation of the film.

A mill is a device that converts energy of external sources (wind, water, mechanical forces) into rotational energy by means of blades. The mill created here might recall the light-powered Crookes radiometer and combined the advantages of plastic materials. To take similarity with the Dutch windmill, we decided to take four blades, which consisted of four **2**-LCN films connected to a rotor free to spin around a fixed axis (Fig. 5). The films were attached to the rotor in such a way that the planar side of each film faced the homeotropic side of the consecutive film. The films **2**-LCN were employed because of their fast dynamics of bending and unbending. By irradiating the blades with focused light, we induced the unidirectional rotation of the mill with a frequency of about 1 Hz (see movie S1, real time video). With the fixation of the blades depicted in Fig. 5, the mechanism of the actuation is as follows: upon exposure the right side of the mill to light, the film bends up at the planar side, in the plane of the mill. This motion has an angular momentum in the direction of the bending causing a counterclockwise rotation of the rotor. The blade rotates and moves out of the light spot, which induces its relaxation. At the same time, this rotation brings a new blade to be exposed to light, which produces again the force leading to the repetition of the rotatory movement. This successive bending/unbending of the different blades over time gives rise to the continuous rotation of the mill in

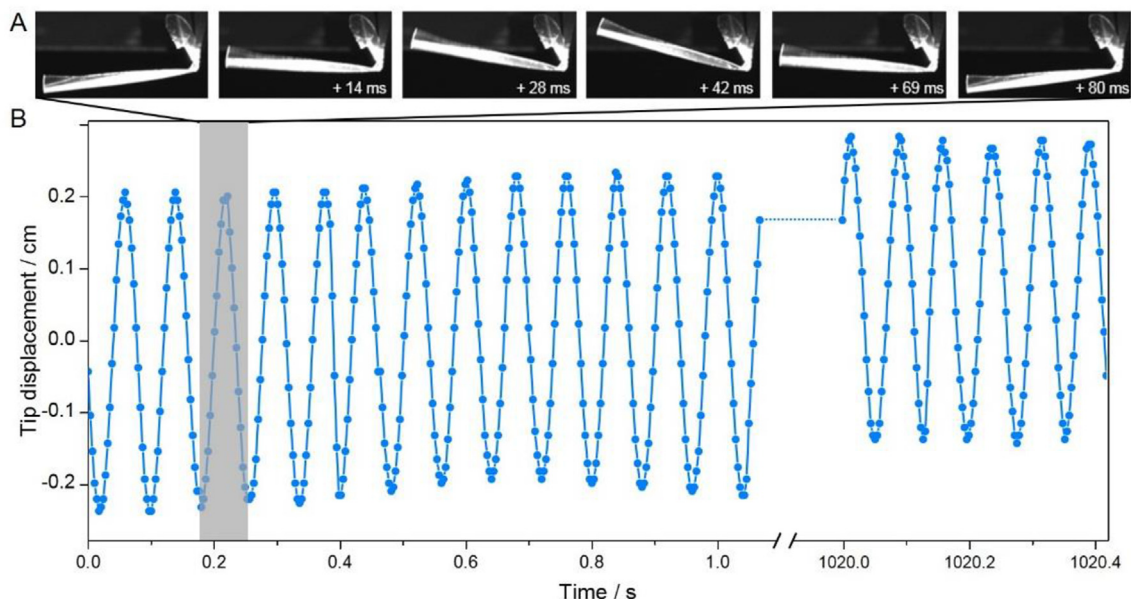


Fig. 4. A) A sequence of frames over irradiation time showing oscillations of the film 2-LCN by continuous light irradiation (405 nm , 0.50 W cm^{-2}). The sample is irradiated from the left and its geometry is 1.2 cm (length) \times 0.4 cm (width) \times $20\text{ }\mu\text{m}$ (thickness). B) The tip displacement of the film 2-LCN over time showing the self-sustained oscillations. The middle position between two extreme positions of the oscillations moved slightly over time ($\sim 0.03\text{ cm}$).

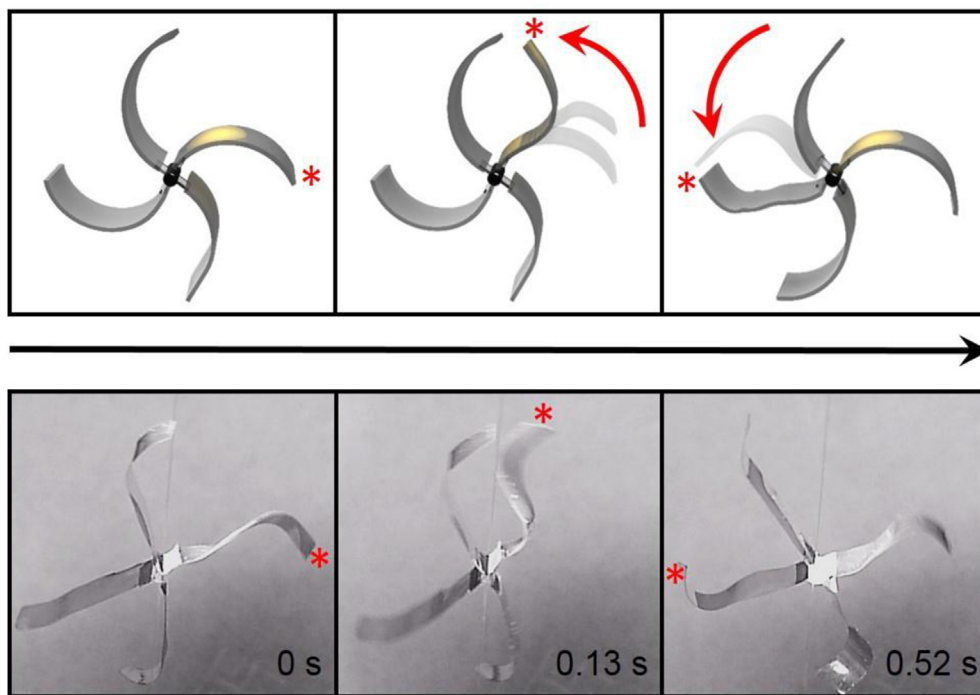


Fig. 5. Schematic representation of the mill turning counterclockwise upon light irradiation (top). The light source is positioned on the top right of the mill and the focus point of the light is represented by a yellow spot on the right blade; Series of photographs showing time profiles of the rotation of the light-driven mill (bottom) (LED 405 nm , 0.50 W cm^{-2} , LCN with $2.5\text{ wt}\%$ of **2**, blade dimensions 1.7 cm (length) \times 0.4 cm (width) \times $20\text{ }\mu\text{m}$ (thickness)).

the same direction. The use of the 2-LCN films is necessary to obtain the constant rotation because of their fast dynamics of bending and unbending, which dis-equilibrates continuously the system and keeps it out-of-equilibrium. One may note that the blades move away from the light beam before they start to oscillate. Remarkably, the direction of rotation of the mill is independent of the direction of illumination because the bending direction does not depend on

the side of the film irradiated, while it depends on the film orientation with regard to the planar and homeotropic sides. The opposite rotation in a clockwise direction was obtained by reversing the mill upside down around the fixed axis such that the film bends down at the planar side upon light exposure. We assume the motion is governed by the weight of the mill and the impulse of the fast bending. As represented in Fig. 5, the curving and then the

uncurving of the blade shift the position of the mill gravity center to the left, which generates a disequilibrium and a rotation counter-clockwise. In addition, the fast bending of the blade generates a punctual acceleration participating in the rotation in the same direction than the weight. At a larger or smaller scale, this concept of the rotating mill will be limited by the intensity and the size of the light spot needed to actuate the blades.

Supplementary video related to this article can be found at <http://dx.doi.org/10.1016/j.tet.2017.06.041>

We have successfully developed out-of-equilibrium macroscopic deformation in LCN films, including a four-blade light-powered mill device which can convert focused light energy directly into mechanical work. The hydrazones employed display interesting features like high stability, no absorption in the visible range and biocompatibility, which broaden their field of applications. Therefore, they present an interesting alternative to azobenzenes and other well-known photo-switches.^{12–15} Furthermore, the possibility to exchange either the carbonyl or the hydrazine units of a hydrazone also offers the intriguing potential to merge collective molecular motion with covalent dynamic materials.²¹

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.tet.2017.06.041>.

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