



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

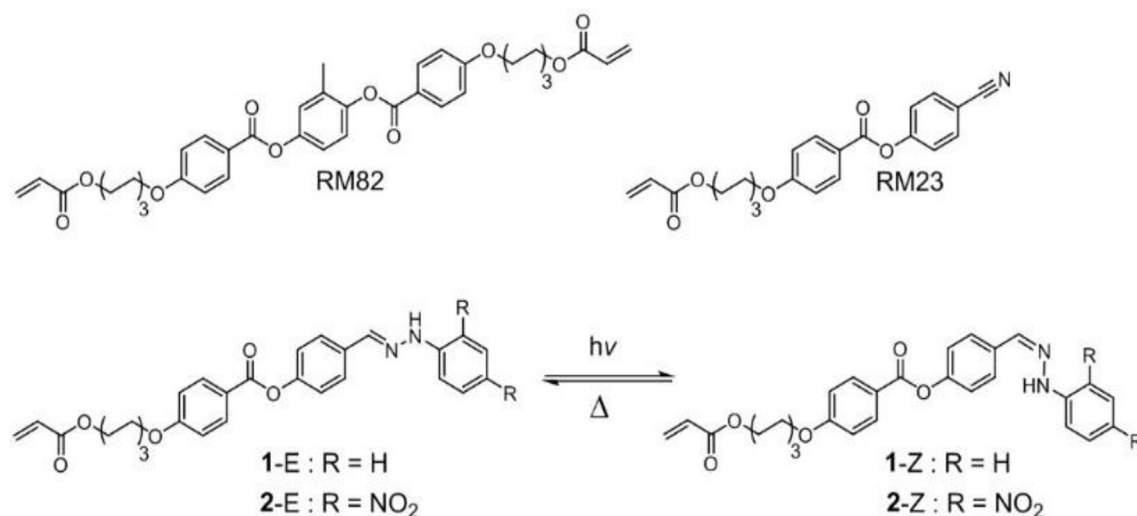


Fig. 1. Mesogens structures and E/Z isomerization of hydrazones **1** and **2**.

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