Molecular Switches **Hot Paper**

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Fluorinated Azobenzenes for Shape-Persistent Liquid Crystal Polymer Networks

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Abstract: *Liquid crystal polymer networks respond with an anisotropic deformation to a range of external stimuli. When doped with molecular photoswitches, these materials undergo complex shape modifications under illumination. As the deformations are reversed when irradiation stops, applications where the activated shape is required to have thermal stability have been precluded. Previous attempts to incorporate molecular switches into thermally stable photoisomers were unsuccessful at photogenerating macroscopic shapes that are retained over time. Herein, we show that to preserve photoactivated molecular deformation on the macroscopic scale, it is important not only to engineer the thermal stability of the photoswitch but also to adjust the cross-linking density in the polymer network and to optimize the molecular orientations in the material. Our strategy resulted in materials containing fluorinated azobenzenes that retain their photochemical shape for more than eight days, which constitutes the first demonstration of long-lived photomechanical deformation in liquid-crystal polymer networks.*

Liquid crystal polymers containing molecular photoswitches have emerged as a promising and exciting class of materials for achieving optical to mechanical energy conversion.[1–3] The actuation of these smart materials is usually driven by the photoisomerization of azobenzene because its *trans*-to-*cis* isomerization proceeds with a geometrical change at the molecular level that disrupts liquid crystallinity and effectively generates disorder. In response, the polymer network deforms anisotropically, with a contraction along the average molecular orientation and an expansion orthogonal to it.[4] Earlier studies have shown the possibility of amplifying the conformational change of azobenzenes to the macroscopic level by integrating these switches into liquid crystal polymer networks.[5] After the irradiation has been stopped, these materials generally recover their original shape within minutes or even seconds.[6] This shape recovery remains difficult to control and constitutes a major hurdle towards practical applications. Shape-persistent liquid crystal polymer networks may give rise to novel materials,[7] for which the morphology could be finely controlled by light, and any given shape that could be reached at an intermediate stage of the process could be preserved. Such materials would find applications in soft robotics, haptics, or biomedical devices, for example, as robotic grippers or as components of artificial muscles.

The use of *ortho*-fluorinated azobenzenes as basic switching elements has the potential to significantly increase the lifetime of photogenerated shapes because the *cis* isomer has a half-life of up to two years in solution (Figure 1).[8,9] Moreover, halogenated azobenzenes absorb in the visible range and can be switched with sunlight when in solution or in liquid crystals.[10] However, designing general principles to translate molecular switching from the nanoscale up to the functional level remains an open challenge,[11] and specifically, in some recent examples, the (macroscale) shape relaxation seemed to be decorrelated from the relaxation of the *meta*-fluorinated azobenzene constituent. White et al. have inves-

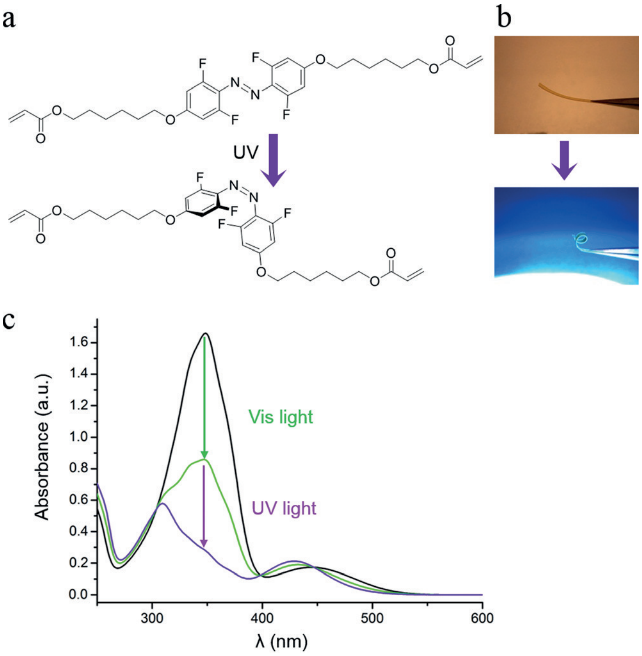

Figure 1. Photoactivation and shape persistence. a) Azo-F photo-isomerizes from the *trans* to the *cis* form under irradiation with visible ($\lambda > 420$ nm) or UV light ($\lambda = 365$ nm). b) A polymer ribbon containing Azo-F curls under UV irradiation and retains its shape. c) UV/Vis absorption spectra showing that Azo-F in dichloromethane switches from the *trans* form to the *cis* form under irradiation with light.

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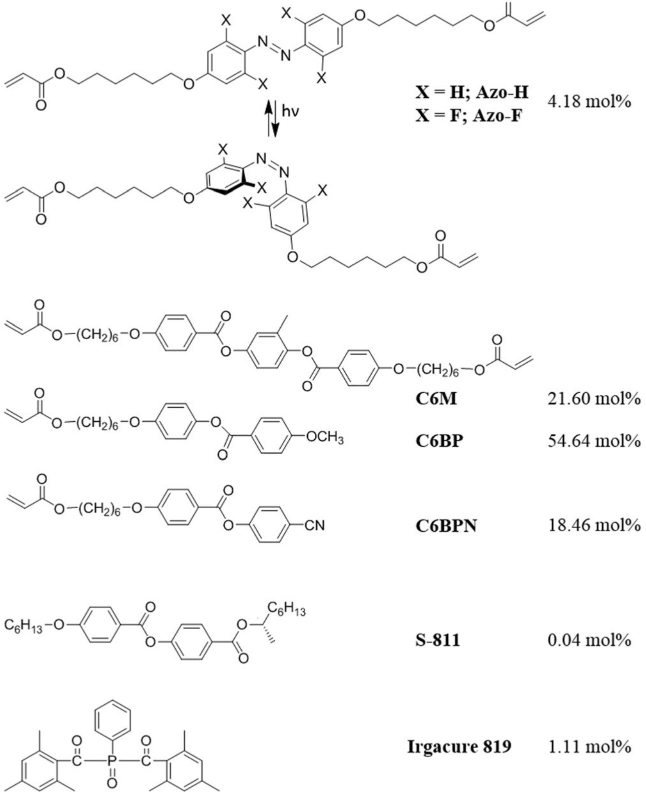
tigated shape changes in a liquid-crystal polymer network containing a *meta*-fluorinated azobenzene.[12] Despite the *cis* form being stable for about 180 h in solution, as soon as irradiation was stopped, the polymer underwent rapid relaxation to its original shape. The amplitude of the deformation was also moderate. This lack of retention in the shape-morphing properties was proposed to arise from 1) possible interference from hydrogen bonding favoring the *trans* form and 2) the lack of order in the liquid-crystal polymer network—implying a random orientation of the switches within the network—which might prohibit effective translation of their shape change into the decrease in order parameters. Herein, we propose that aside from these contributions, the nature of the coupling between the photoswitch and its environment is a major factor in determining the macroscopic shape-shifting properties of the material. For example, main-chain liquid-crystal polymers produce stronger thermomechanical effects than side-chain systems.[13] Other investigations have suggested that combining a low cross-linking density with a uniform cross-linking distribution is key to designing shape-memory polymers.[14] Thus we anticipated that the cross-linking density would have to be adjusted. In liquid crystal polymer networks actuated by azobenzenes, the cross-linking density reduces the *trans*-to-*cis* photoconversion[15] and attenuates shape-memory effects by promoting a faster relaxation of the network.[16] Moreover, it is known that azobenzene moieties relax faster when they are strained.[17] In a highly cross-linked polymer network, it is likely that the azobenzenes are strained, especially when a short spacer is used to separate the mesogenic core unit from the reactive end groups.[18]

We designed a liquid-crystal polymer network that contains a low ratio of diacrylate cross-linkers and in which the cross-linkers have a longer spacer (Scheme 1). We anticipated that the coupling between the switches and their environment would be sufficiently weak to allow for efficient *trans*-to-*cis* photoisomerization of *ortho*-fluorinated azobenzenes, and strong enough to overcome the elastic properties of the network and control the kinetics that restore the object to its initial shape. Other limiting factors were attenuated or suppressed by diluting the switch within the network down to 5 wt% of the material only, and by relocating the fluorinated switch to the main polymer chain. Recent work on surface morphing has indeed reported that diacrylate azobenzenes used as cross-linkers induce larger-amplitude shape changes than azobenzene monoacrylates.[6] Our strategy resulted in liquid crystal polymer networks that undergo large photoinduced deformations and keep the shape of any given state for days.

We synthesized the *ortho*-fluorinated azobenzene Azo-F, which contains two reactive end groups, and its classical counterpart Azo-H for comparison (Scheme 1; see also the Supporting Information, Figure S1). A liquid crystal polymer film was prepared by photopolymerization of a nematic liquid crystal ($\lambda > 420$ nm) containing one of the reactive monomers, namely Azo-F or Azo-H, about one percent of the photoinitiator (Irgacure 819), and trace amounts of a chiral dopant (S-811) in a glass cell promoting a twist geometry for the liquid crystal. A step-by-step procedure describing how liquid-crystal polymer networks can be optimized to form spring-like macroscopic geometries and the preparation of these materials are reported elsewhere.[19,20] It should be noted that the use of a twist geometry is particularly suitable for studying shape changes because liquid-crystal polymer films with a twisted or splayed organization display larger-amplitude shape shifting than similar films with a planar organization of the director.[21]



Scheme 1. The photoswitches Azo-H and Azo-F. Two reactive end groups enable the incorporation of the switches as cross-linkers into the network. Aside from the photoswitches, the polymer matrix was built from the reactive mesogens C6M and C6BP as well as C6BPN, which bear two and one polymerizable end groups, respectively. The chiral dopant S-811 was used to promote a left-handed twist in the film, and the photoinitiator Irgacure 819 was used for photo-polymerization at $\lambda > 420$ nm. Other compositions that were tested include the same composition as in Ref. [20]; however, the film displayed poor elastic properties.

The photoisomerization and relaxation processes of the switches embedded covalently in the liquid-crystal polymer film were studied by UV/Vis absorption spectroscopy. Comparing their relaxation rates in the dark revealed that the thermal relaxation of *cis*-Azo-F to *trans*-Azo-F is slower than that of *cis*-Azo-H. After two days, the characteristic absorption band of *cis*-Azo-F was still observed whereas Azo-H embedded in the network showed nearly full conversion of the *cis* isomer into the *trans* isomer over the same period of time (Figure 2). The thermal stability of *cis*-Azo-F was further confirmed by ^{1}H NMR spectroscopy (Figure S2).

The shape recovery of springs containing either Azo-H or Azo-F was then investigated. We cut ribbons out of liquid-

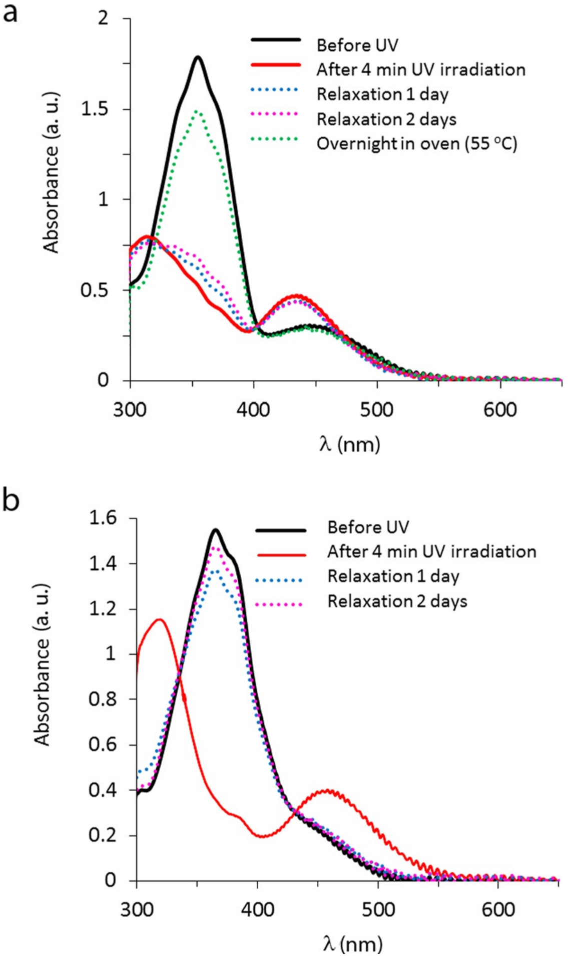


Figure 2. Photoswitching ($\lambda = 365$ nm) and thermal relaxation of a) Azo-H and b) Azo-F incorporated covalently into thin films of liquid crystal polymer networks. For the spectroscopic investigations, the nominal gap of the cells was 15 μm.

crystal polymer films with a twist-nematic organization, in a cutting direction that is defined by the angle φ (Figure 3 a), defined as the angle between the orientation of the molecules at mid-plane on one hand, and the long axis of the ribbon on the other hand. For $\varphi = 90°$, the Azo-F ribbon relaxes more slowly than the Azo-H ribbon: After two days, the Azo-H based film was nearly half way back to its original shape whereas the film containing Azo-F showed only minor shape changes (Figure 4). However, this comparison was hampered by the fact that the photodeformation of ribbons incorporating different switches was not the same, despite being characterized by the same angle φ (Figure 3 b). In previous work, we had shown that the shape of the springs is determined by the cutting angle, the handedness of the twist in the cell, and the gradient in the cross-linking density.[20] Here, apart from the switches Azo-F and Azo-H themselves, the films have the same composition. The fact that different springs are formed for the same cutting angle is likely related to the formation of different profiles for the gradient in the cross-linking density that runs through the thickness of the sample, as the switches have different concentrations and also different absorption coefficients.

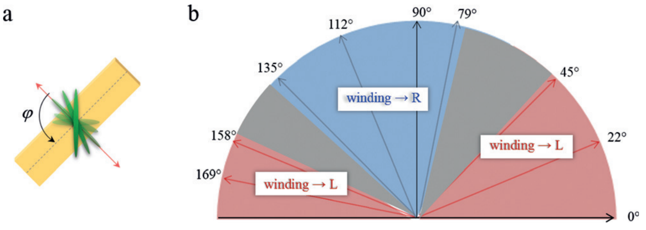


Figure 3. a) The angle φ is defined as the angle between the preferential orientation of the molecules at mid-plane and the long axis of the ribbon. b) Shape and actuation modes of the polymer springs containing Azo-F as a function of the angle φ. The nominal thickness of the ribbons was 50 μm.

Consequently, we studied the shape recovery of objects that contain either Azo-F or Azo-H and have identical macroscopic geometries, which means that the molecular organization in the ribbons is different because Azo-F and Azo-H networks produce different shapes. Ribbons with similar macroscopic shapes and deformations were selected from our library of photoresponsive springs (Figure S3). Specifically, we chose ribbons that bend and compared the rates of their shape recovery in the dark (Figure 5). Within a week after irradiation with UV light, a ribbon cut out from a thin film containing Azo-H ($\varphi = 0°$) recovered its original shape. In contrast, a flat ribbon containing Azo-F ($\varphi = 112.5°$) was transformed into a bended shape under illumination with UV light, and remained bent for at least eight days, that is, the photogenerated shapes of Azo-F displayed long persistence.

For the specific Azo-F spring cut at $\varphi = 112.5°$, we observed a time delay before the full amplitude of the photomechanical response of the Azo-F network was reached, which was not reported in earlier investigations. Specifically, comparing Figure 5 iii and Figure 5 v, we note that the material incorporating Azo-F continues to bend even after UV irradiation has been stopped. Importantly, this lag was not observed for all cutting angles, its origin remains to be investigated.

The system showed another kinetic difference between the dynamic behavior of Azo-H and Azo-F once incorporated into the network and the macroscopic shape relaxation. Specifically, the shape relaxation of the liquid-crystal network is slower than the *cis*-to-*trans* relaxation of Azo-F: Overall, the material relaxes even more slowly than the fluorinated azobenzenes that it contains (Figure 4 b, c). A kinetic lag has recently also been reported for the surface morphing of liquid-crystal elastomers.[6] Specifically, a kinetic mismatch was observed between the slower azobenzene relaxation and the faster relaxation of the polymer network in systems where the relaxation rate was dominated by the viscoelastic deformation of the polymer network rather than by the photochemistry of the switch. Here, Azo-F responds more quickly than the polymer network into which it has been incorporated, both during the photo-step and during relaxation. We anticipate that this behavior arises from a lag in the gradual reorientation and subsequent reorganization of the polymer that incorporates the photo-switches.

In summary, Azo-F units has been covalently incorporated into liquid-crystal polymer networks as switchable

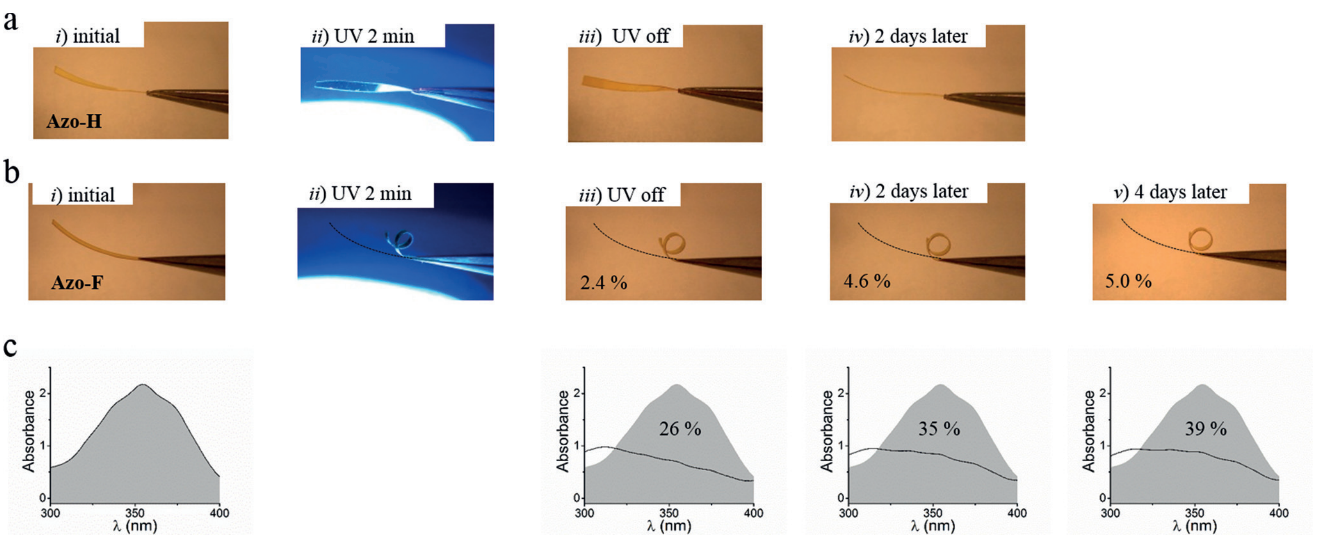


Figure 4. Irradiation and thermal relaxation of ribbons cut at an angle $\varphi=90°$ out of a thin film containing a) Azo-H or b) Azo-F as the active switching unit. The percentages of shape recovery are specified in the bottom left corner of the pictures. The dashed line is a guide for the eye, to compare the curled ribbon with a reference. c) UV/Vis absorption spectra and percentage of the *trans* recovery of the Azo-F switch in the ribbon.

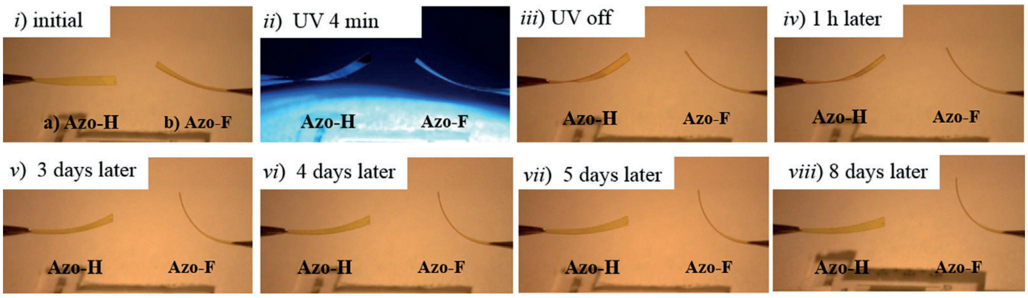


Figure 5. Irradiation and thermal relaxation of ribbons cut from a film containing a) Azo-H ($\varphi=0°$) or b) Azo-F ($\varphi=112.5°$). The cutting angle was chosen in such a way that the ribbons are flat initially and bend under irradiation. The nominal thickness of the ribbons was 50 μm.

cross-linkers. These dynamic units performed well in transducing light into complex mechanical function, and the shape of the Azo-F network was retained for a long period of time (> 8 days). The composition of the polymer matrix was key in preserving photoactivated molecular deformation on the macroscopic scale. We also showed that for some compositions and geometries, the response of the polymer network lags behind the molecular switching in both directions, showing similarities with a hysteresis behavior. Our results finally suggest possible developments towards responsive materials displaying phototropism, because in solution, *ortho*-fluorinated switches can also be activated by visible light (Figure 1).[8] Overall, these results demonstrate that molecular photoswitches can be engineered to overcome thermal relaxation, and that the coupling between these switches and their environment remains key to harnessing molecular photoswitching when designing soft machines by converting light into mechanical work.

Experimental Section

The synthesis of Azo-H and Azo-F is described in the Supporting Information. The liquid crystals were purchased from Synthon Chemicals. The chiral dopant S-811 and the photoinitiator were supplied by Sigma-Aldrich. HPLC-grade dichloromethane was used for the preparation of the liquid crystal mixture. Liquid crystal cells were purchased from E.H.C. Co., Ltd, Japan.

The liquid-crystalline base composition mixture contains (mol %) 4.2 % of the azobenzene switch (either Azo-F or Azo-H), 94.7 % of liquid crystal monomers (C6M/C6BP/C6BPN in a molar ratio of 1.17:2.96:1), 0.038 % of the chiral dopant (S-811), and 1.1 % of the photoinitiator (Irgacure 819). The amount of chiral dopant S-811 was adjusted to induce a 50 μm quarter pitch. All components were brought together by dissolution in dichloromethane; then the solvent was evaporated at 60 °C under a nitrogen stream. Afterwards, the liquid crystal was heated up to the isotropic phase (80 °C) for 30 min, then gradually cooled down to obtain the nematic phase (48 °C), injected into the liquid-crystal cell, and left at 48 °C for 1 h before photopolymerization with visible light for 3 h using an Edmund MI-150 high-intensity illuminator equipped with a cut-off filter ($\lambda \geq$ 420 nm, 77–170 mW cm^{-2}). The polymerized film was retained in the cell at 55 °C overnight for optimal polymerization.

The nominal gap of the twist cells was 50 μm, and the nominal gap of the planar cells was 15 μm. The ribbons were cut from the twist cells with a scalpel. Their typical dimensions were approximately 1 mm × 6 mm × 0.05 mm.

The UV/Vis absorption spectra were recorded using a Perkin-Elmer Lambda 850 UV/Vis spectrophotometer. Shape changes were captured with a Dino-Lite Pro AM4113T USB microscope.

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