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# Photo-Controlled Dynamics of Cholesteric Polymer Coatings via Hydrazone Crosslinking

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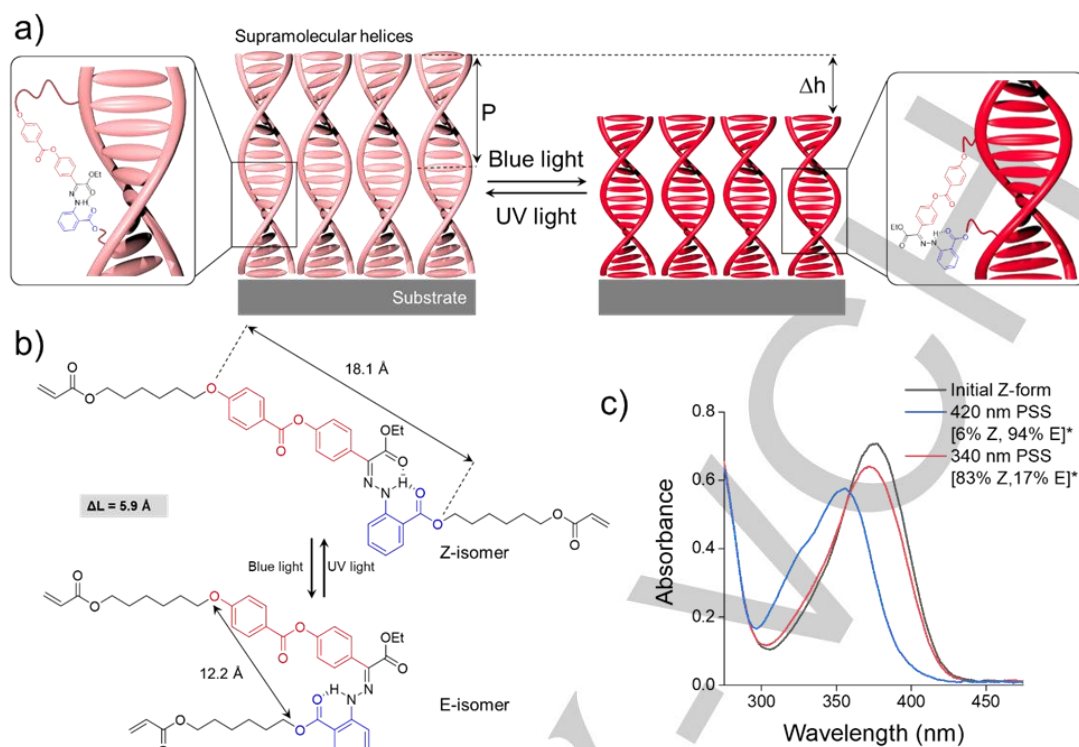
**Abstract:** Developing responsive coatings and smart materials requires discovering a breadth of mechanisms by which external stimuli can be converted into useful signals. Here, we demonstrate an approach driven by supramolecular mechanochemistry, where mechanical input—molecular shape change—is translated into structural color variation. By embedding bistable, negatively photochromic hydrazone photoswitches into cholesteric polymer networks, we achieve a reversible, stable color shift through molecular-scale pulling and pushing of the photonic scaffold. Unlike azobenzene-based systems, which typically disrupt liquid crystal order, this approach modifies the pitch of a crosslinked cholesteric helix without loss of structural integrity. The long-lived bistability of both hydrazone isomers ensures durable optical switching. This concept provides a new strategy for designing mechanoresponsive photonic coatings and tunable optical materials.

The understanding and subsequent use of the mechanisms of dynamic transduction of information from molecular to micro- and macroscopic length scales in novel intelligent materials has garnered much attention in the past decade.<sup>[1,2]</sup> The main motivation behind this research focus is the need to push modern materials science to the next level by designing artificial materials that not only possess a number of passive useful properties (e.g., color, elastic modulus, viscosity, etc.) but can also perform more sophisticated tasks, such as responding to external stimuli, adapting to environmental conditions and even performing computational tasks. In pursuing this goal scientists have been taking inspiration from natural (biological) materials

where the operation of small molecules and molecular motors govern the properties and functions of bulk materials through a complex network of hierarchical supramolecular organization. As a man-made counterpart of these biological active molecules one can consider artificial molecular switches and rotary motors as the triggers that can ultimately be using in mimicking biological functions.<sup>[3-7]</sup> Such molecules can undergo considerable structural changes, and in a reversible manner, when interacting with appropriate stimuli, which can in general be either light or chemical reactants. Despite recent advances in the synthesis of molecular switches and artificial motors, one of the main challenges in the field is in the development of principles for transforming molecular structural changes into useful functionalities that transpire on larger scales, which is a requirement for developing actuators and soft robotics, as examples.

Here we report on optical coatings, where the driving mechanism is the operation of a negatively photochromic hydrazone.<sup>[8,9]</sup> The geometrical photoswitching of the hydrazone is transformed into dynamic color change of the polymer coating by means of multiscale hierarchical design, where the photoswitch is covalently incorporated into the periodic supramolecular helical architecture of a liquid crystal (LC).<sup>[10]</sup> The LC is responsible for the structural coloration of the coating and a similar principle of coloration can be found in Nature (e.g., the color of butterfly and bug wings, feathers, chameleon skin, etc.) and can be described by the following equation (Eq. 1):

$$\lambda_{\max} = nP \quad (1)$$



**Figure 1.** a) Hydrazone photoswitches integrated in a cholesteric liquid crystal polymer network. The change of shape of the hydrazone drives the contraction/expansion of the network and associated change of pitch in the helix. b) Reversible photo-induced *Z/E*-isomerization of the artificial molecular switch. The photoisomerization is accompanied by large geometrical changes of the molecular switch, with a difference in molecular length  $\approx 0.6$  nm. [Erreur ! Signet non défini.] c) Absorbance spectra of *E* and *Z* isomers of hydrazone obtained photochemically by exposure of chloroform solution to blue ( $\lambda = 420$  nm) and UV light ( $\lambda = 340$  nm), respectively. \* Exact *Z/E* ratios were obtained by  $^1\text{H}$  NMR spectroscopy analysis.

where  $\lambda_{\text{max}}$  is the center of reflection band,  $n$  is the average refractive index, and  $P$  is the supramolecular pitch. As evident from Eq. 1 the reflected color ( $\lambda_{\text{max}}$ ) is fully governed by the periodicity of the cholesteric helix ( $P$ ) which, in turn, is determined by the chirality of the molecules (dopants) inducing a cholesteric mesophase. Molecular photoswitches and rotary motors have been successfully used in controlling  $P$ , and consequently colors of a material though the modulation of the helical twisting power (HTP;  $\text{HTP} = 1/P^*c$ , where  $c$  is concentration of chiral dopant).<sup>[11,12]</sup> Despite the efficiency of this approach it is only applicable for liquid materials since it requires the rearrangement of supramolecular helices through the modulation of the structure of the chiral dopants.<sup>[13-15]</sup> On the other hand in cross-linked polymeric systems the helical rearrangements are hindered by covalent networks, and account for a set of mechanical and photophysical properties which allows their use as, e.g., coatings. For cross-linked cholesteric systems we suggest considering Eq.1 in a different way:

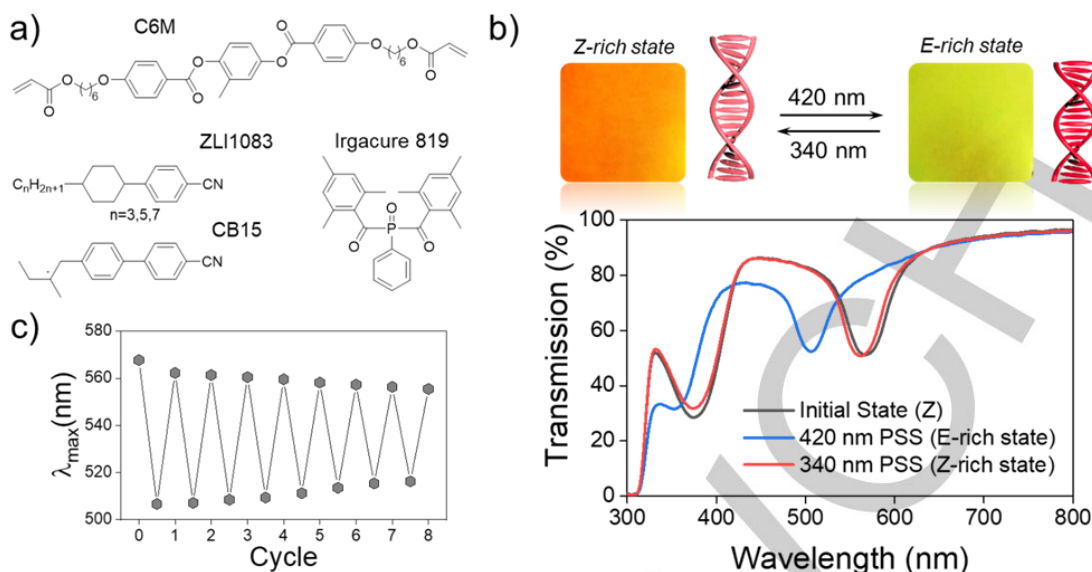
$$\lambda_{\text{max}} = nh/N \quad (2)$$

where  $h$  is the thickness of the layer/coating and  $N$  is the number of full turns of a cholesteric helix, i.e.,  $P=h/N$ . It is clear then that the covalent network imposes certain restrictions, namely  $N$  is constant and cannot be changed. Consequently, the modulation of thickness ( $h$ ) provides a way to control the color of the layer/coating. Herein we show how hydrazone photoswitches can be used in varying the thickness of helical polymer layers (Figure 1a) and subsequently tuning their colors. We used a previously designed hydrazone diacrylate<sup>[16]</sup> for shape encoding and actuating the polymer films (Figure 1b).

This hydrazone is negatively photochromic with a thermodynamically stable *Z*-form. Initially, the yellowish *Z*-hydrazone isomerizes to colorless *E*-form (Figure 1c, see details in Supporting Information, Figure S1-S2) upon blue light exposure (420 nm). Back isomerization can be accelerated by UV illumination (340 nm) while thermal relaxation under dark is almost completely hindered, as the half-life of the *E*-form is thousands of years.<sup>[17,18]</sup> The ratios of *Z* and *E* forms obtained in the photostationary state (PSS) are shown Figure 1c.

The hydrazone diacrylate (3 wt.%) was integrated into the cholesteric network obtained by the photocrosslinking of a cholesteric monomeric mixture consisting of mesogenic diacrylate (C6M, 5 wt.%), low molar mass liquid crystals (ZLI1083, 62 wt.%), chiral dopant (CB15, 30 wt.%) and traces of the photoinitiator Irgacure 819 (Figure 2a). The details of the cholesteric coating preparation as well as the data regarding how the composition of the coating affects its optical performance are discussed in the Supporting Information (Figure S3).

The as prepared cholesteric coating is orange colored because of the selective light reflection from the periodic helical structure. The light reflection appears as a band in the transmission spectrum centered at about 570 nm (Figure 2b). Irradiation of this coating with blue light (420 nm) causes a fast color shift, and the coating turns yellow (reflection  $\lambda_{\text{max}} \sim 505$  nm). Further irradiation with UV light (340 nm) shifts the band to almost the initial state, restoring the initial color of the coating. The kinetic curves of the color modulations are shown in Figure S4 (see Supporting Information). It is worth noting that if the cholesteric layer is confined between two glass substrates, the



**Figure 2.** a) Components of the cholesteric liquid crystal polymer network. b) Reflection colors of the cholesteric network containing hydrazone cross-linker upon light exposure (on top) and corresponding transmission spectra (bottom). The size of the images on top is  $1 \text{ cm}^2$ . c) Reversibility of the color change (position of selective light reflection peak,  $\lambda_{\text{c}}$ ) during cycling illumination between blue (420 nm) and UV (340 nm) light.

reflection band is not sensitive toward light illumination (Figure S5). However, if one side of the layers is free and unconstrained, the network can contract/expand without any constraints, and consequently change color.

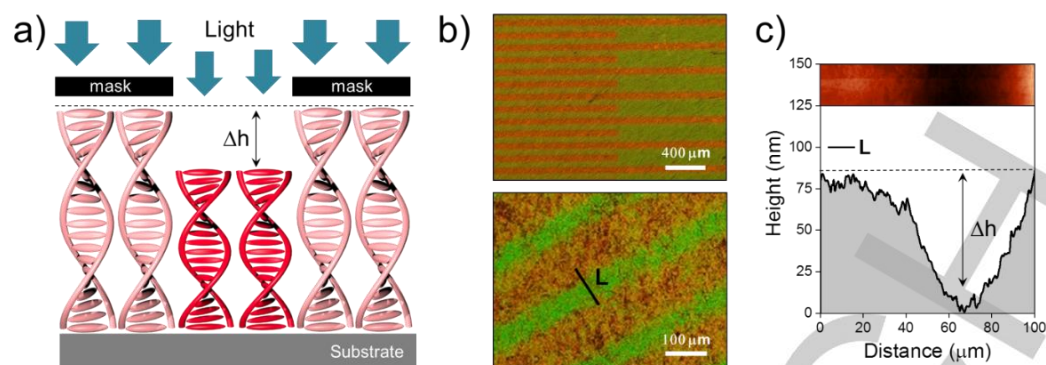
The reversible color shift ( $\Delta\lambda_{\text{max}}$ ) of 65 nm solely originates from the large molecular shape change of the hydrazone (Figure 1b) caused by *Z-E* photoisomerization. Because of the geometrical constraints of the glass substrate (i.e., the layer cannot contract/expand in the plane of the substrate) this molecular shape change pulls on the network thus contracting it in the direction of the coating normal, i.e., modulation of layer thickness. Since the number of turns of cholesteric helix is fixed by the network upon photopolymerization, the decrease in thickness of the layer results in the shortening of the cholesteric pitch, and consequently the color of the layer shifts to the blue spectral region. The opposite happens when the thickness of the layer increases upon UV light irradiation. This process of color change is reversible and can be repeated many times (Figure 2c, Figure S6) yielding moderate narrowing of the spectral modulation range, likely because of the partial expulsion of free liquid crystal fraction from the network.<sup>[19,20]</sup>

The design of the hydrazone switch allows its operation without causing disruption of the liquid crystalline order, as we have demonstrated previously (see also discussion in Figure S7).<sup>[Erreur ! Signet non défini.]</sup> Hence, the large molecular shape change upon photoisomerization is responsible for the building up of mechanical strain in the network which causes its contraction/expansion. Since the manipulation of the color is a photochemically driven process, and the *E/Z* isomer ratio can be manipulated as a function of wavelength or irradiation time photostationary state, any color in the spectral modulation range can be obtained, and importantly they can be locked in thanks to the extraordinary stability of the *E*-hydrazone. For example, even after storing (in the dark) a sample pre-exposed to blue light for as long as a year, no visible color change was observed, and the color was still changeable by UV exposure.

One can argue that similar effects can be achieved by using conventional azobenzene switches. To address this question we

prepared similar cholesteric coatings containing fluoro-substituted azobenzene with very stable *Z*-form.<sup>[21]</sup> Our results (see Supporting Information, Figure S8 and S3) show that the azobenzene switch only allows a transmission band shift of 14 nm, which can be explained by the smaller molecular shape change (0.35 nm vs 0.59 for hydrazone) and reduction of the liquid crystalline order by *Z*-azobenzene.<sup>[22]</sup> The latter effect usually causes expansion of the networks,<sup>[23]</sup> which interferes with the contraction driven by the molecular shape change. On the other hand, the hydrazone switch designed by us does not affect the liquid crystalline ordering and therefore it generates a larger molecular change, resulting in around 5-fold difference in color shift. This observation attests to the unique benefit of the hydrazone switch, which combines, large geometrical change and bistability with order-to-order transitions in bulk materials.<sup>[24-31]</sup>

To prove that *Z/E* isomerization of the hydrazone indeed results in contraction of the network and reduction of its thickness, we studied the affected surfaces with AFM. We used a photomask with transparent and non-transparent stripes to impart topography on the cell surface topography using blue light exposure. Such patterning results in the alternation of exposed areas where the network contracts, and unexposed areas with native state of the network (Figure 3a). Figure 3b demonstrates the obtained color pattern observed by polarized light microscopy in reflection mode (see also Figure S9). The surface study of the stripe-patterned coating performed by AFM revealed a thickness modulation as high as 75 nm (Figure 3c). From Eq. 2, the expected modulation of the thickness is about 200 nm, considering an initial thickness of the coating of  $2 \mu\text{m}$  and an average refractive index of 1.5. The lower experimental value can be explained by the partial erasure of the pattern because of the back *E/Z* isomerization of the hydrazone induced by the exposure to ambient (room) light during the experiments.



[6] T. van Leeuwen, A. S. Lubbe, P. Štacko, S. J. Wezenberg, B. L.

**Figure 3.** a) Recording of optical patterns on hydrazone-based dynamic cholesteric networks. Irradiation of the cholesteric layer through a mask results in spatial modulation of the thickness and consequently color. b) Optical image of the striped pattern and the AFM surface profile c) along the track 'L', which displays the thickness drop in areas exposed to blue light. Corresponding AFM scan (25 μm width) is on top of figure c.

In conclusion, we have demonstrated a supramolecular mechanochemistry approach to tunable optical coatings, where molecular shape changes in a hydrazone photoswitch translate into mechanical contraction of a network, and further into structural color variation. The contraction of the cholesteric polymer network is due to the tension applied by the hydrazone switch, and alters the pitch without disrupting the liquid crystal order. Unlike azobenzene-based systems, which operate by a combination of both tension and order disruption in the soft matter system, our approach to optical response preserves the integrity of the photonic scaffold while enabling reversible and durable color switching. The stability of both Z and E forms of the hydrazone ensures long-term bistability, allowing for multiple cycles of actuation. We envision that this strategy—harnessing molecular-scale mechanical inputs to control optical properties—can inspire new classes of responsive photonic coatings and tunable optical materials.

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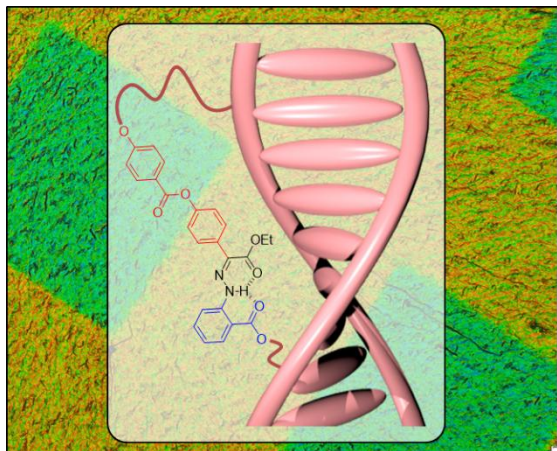
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## Entry for the Table of Contents



Here we present innovative approach which integrates responsive molecules into larger ensembles, resulting in photo-controllable and -patternable color. By covalently coupling hydrazone photoswitches with supramolecular helical polymer networks, we harness light-driven molecular shape changes to modulate structural color. Our multi-length scale design enables macroscopic level function and potential applications in tunable photonics and optics.