

Reversible Full-Range Color Control of a Cholesteric Liquid-Crystalline Film by using a Molecular Motor

Rienk Eelkema and Ben L. Feringa*^[a]

Abstract: By using a chiral molecular motor as a dopant in a cholesteric liquid-crystalline film, fully reversible control of the reflection color of this film across the entire visible spectrum is possible. The large difference in helical twisting power between the two isomeric forms of the motor allows efficient light- and heat-induced switching of the helicity of the cholesteric liquid-crystal superstructure.

Keywords: chirality • color • liquid crystals • molecular devices • photochromism

Introduction

Dynamic control of a change in color is a key feature of modern information technology. It allows visual readout of a signal and is used extensively in, for instance, liquid-crystal (LC) color displays, television monitors, and sensors. LC color-display technology relies on the selective transmittance of light by aligned helically ordered liquid crystals, with pixels that consist of combined red, green, and blue LC cells that have to be addressed separately and by an electronic stimulus to generate the desired colors.^[1] A single colored LC matrix addressable by light would be an attractive alternative as the dimensions of such a pixel would be limited only by the dimensions of light. Furthermore, construction costs might be reduced as it would require one cell per pixel instead of three. Based on the principle of selective light reflection by cholesteric liquid crystals, we describe herein a system in which the entire visible spectrum can be addressed in a reversible manner by using light. The system consists of an aligned cholesteric liquid-crystalline film composed of an achiral mesogenic host and, as a guest compound, a chiral light-controlled molecular motor.

Results and Discussion

Aligned cholesteric liquid crystals with a helical superstructure resulting from the presence of a chiral dopant can reflect light selectively when the length of their helical pitch (p) is of the same order of magnitude as the wavelength of visible light.^[2] The selective reflection is of a Bragg type,^[3] resulting from the repetitive helical order in the cholesteric phase. The wavelength of reflection (λ) depends on the average refractive index of the material (n), the angle of the incident light (α), and the pitch (p), which in turn is inversely proportional to the helical twisting power (β), concentration (c), and enantiomeric excess (ee) of the chiral dopant [Eq. (1)].

$$\lambda_{\alpha} = np \cos(\sin^{-1}(\frac{\sin \alpha}{n})) = n(\beta c e e)^{-1} \cos(\sin^{-1}(\frac{\sin \alpha}{n})) \quad (1)$$

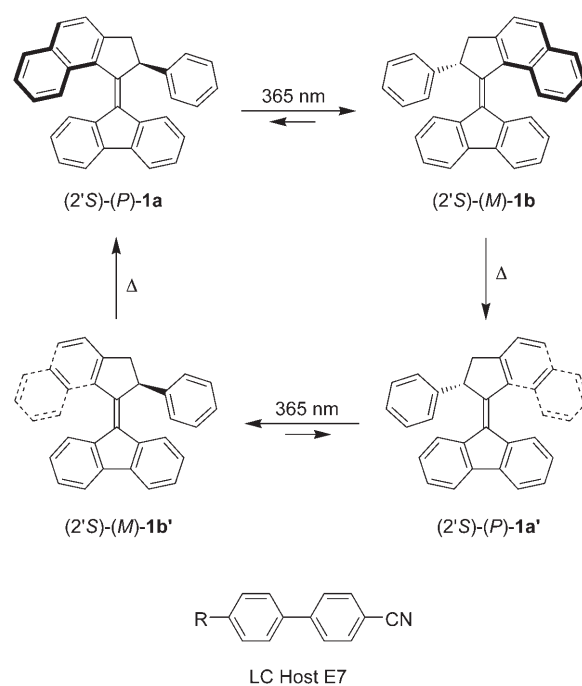
An LC matrix in which the helicity can be manipulated by light can be constructed by using a photochromic dopant that changes conformation upon irradiation, thus influencing the alignment of its surrounding LC host molecules.^[4,5] Chiral photoswitchable dopants are particularly attractive as they offer the possibility of control of the color of LC films with only small amounts of chiral compound.^[6] As the color depends on the helical twisting power, photochemical color manipulation across the entire spectrum requires a significant difference in helical twisting power between the various states of such a switchable chiral dopant. Furthermore, to obtain colors without the use of auxiliary chiral dopants, the chiral switch has to have sufficient solubility in the LC host material, and it is required that at least one of its isomers has a high helical twisting power. Finally, the switching pro-

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cess has to be fully reversible in the LC host at the operating temperature (preferably room temperature). So far, no system that satisfies all these requirements has been described. There have been reports of low- and medium-molecular-weight systems that use auxiliary chiral nonphotochromic dopants or mesogens to obtain reversible full-range color control.^[4,7] Without the use of auxiliary chiral dopants, most systems are only capable of covering part of the visible spectrum.^[8] A polymeric LC material has shown full-range color control, although the system is irreversible.^[9] Recently, we reported a host–guest system that used a molecular motor as a chiral switchable dopant.^[10] Due to the large differences in helical twisting powers between the different states of the motor, the entire visible spectrum could be addressed. However, owing to the intrinsic high isomerization barriers of the motor system at room temperature, these color changes were not reversible. The new chiral switchable dopant presented here allows for the first time reversible color control across the entire visible spectrum without any other sources of molecular chirality present.

Under irradiation with UV light ($\lambda = 365$ nm) at room temperature, chiral dopant (2'S)-(P)-**1** functions as a molecular motor due to a series of photochemical double-bond isomerizations and thermally induced helix inversions (Scheme 1). Important design features of motor **1** are a *P*-helical structure, a single stereogenic centre in the upper part, a central carbon–carbon double bond that functions as the axis of rotation, and a symmetrical lower part.^[11] The fluorene moiety was chosen for the lower part because it has a structural resemblance to the biphenyl LC host compound E7 (Scheme 1) and therefore might enhance the interactions of **1** with the LC host. In its stable form **1a**, the phenyl substituent adopts a pseudoaxial orientation to avoid steric repulsion with the fluorene lower half. Upon irradiation with UV light (365 nm), a photochemical isomerization



Scheme 1. Molecular motor **1** and the structure of the E7 LC blend ($R = n\text{C}_5\text{H}_{11}, n\text{C}_7\text{H}_{15}, n\text{C}_8\text{H}_{17}\text{O}, 4'-n\text{C}_5\text{H}_{11}\text{C}_6\text{H}_4$).

around the central double bond occurs with inversion of the helicity of the molecule ((*P*)-**1a** → (*M*)-**1b**). Simultaneously, the exocyclic phenyl substituent is forced to adopt a strained pseudoequatorial orientation due to a change in conformation of the five-membered ring. A subsequent thermal helix inversion (*M* → *P*), governed by release of this strain, occurs readily at room temperature ($t_{1/2} = 9.9$ min in toluene), leading to stable (*P*)-**1a'**.^[11] Since **1a** and **1a'** are degenerate forms, this sequence can be considered as the first 180° part of the rotary cycle.

Motor (*P*)-**1a** has a high β value of $+90 \mu\text{m}^{-1}$ when dissolved in liquid crystal E7.^[12] Irradiation of (*P*)-**1a** with 365-nm light generates (*M*)-**1b**, which at its photostationary state (PSS) has an effective β value of over $-59 \mu\text{m}^{-1}$, thus indicating that the helicity of the cholesteric phase is inverted (see Supporting Information). When the irradiation is ceased, a β value of $+90 \mu\text{m}^{-1}$ is regenerated after 45 min due to the thermal helix inversion of the motor ((*M*)-**1b** → (*P*)-**1a'**). This process has been repeated over 20 times without loss of helical twisting power. Because of these enormous differences in helical twisting power between the stable form **1a** and the PSS, as well as its thermal reversibility, motor **1** was applied in the generation of photoaddressable colored LC films. First, a rough estimate of the refractive index was obtained by mixing **1a** (5.5 wt %) with E7 on an aligned surface (see Supporting Information). This resulted in a greenish LC film, which indicates a refractive index of around 1.5. By applying this refractive index in Equation (1), the dopant concentration for full color switching was determined to be 6.8 wt %. When this mixture of **1a** and E7 was applied on a linearly rubbed polyimide-covered glass plate, a violet LC film was obtained that was stable for

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Ben L. Feringa obtained his PhD in 1978 at the Univ. of Groningen in The Netherlands. After working as a research scientist at Shell, he was appointed full Prof. at the Univ. of Groningen in 1988 and the Jacobus H. van't Hoff Prof. of Molecular Sciences in 2004. He was elected a member of the American Academy of Arts and Sciences (foreign honorary) and the Royal Netherlands Academy of Sciences, and has received several awards (e.g. Körber, Prelog Medal, Spinoza). His research interests include stereochemistry, organic synthesis, asymmetric catalysis, molecular switches and motors, self-assembly, and nanosystems.

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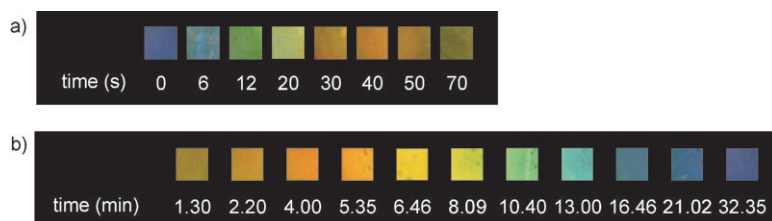


Figure 1. Color change with time of an LC film of E7 doped with molecular motor **1** (6.8 wt %) a) upon irradiation with 365-nm light and b) during thermal helix inversion. The depicted colors are photographs of the LC sample taken perpendicular (90°) to the surface of the film, recorded at room temperature during both processes.

over 5 days. Irradiation of this film with 365-nm light resulted in a rapid color change across the entire visible spectrum (Figure 1 a). After 70 s of irradiation, first a red and then ultimately a slightly yellow film was obtained. This yellow color was caused by the absorption of **1** (see Supporting Information).^[11] Upon removal of the lamp, the film displayed a slow hypsochromic shift. Over the course of 33 min the color changed from red to yellow, green, and blue, eventually reverting to the starting point violet (Figure 1 b). This process was repeated several times to show the reversibility and fatigue resistance of the system. Also, gentle heating of the sample resulted in a faster reverse process, which is to be expected as the conversion from unstable (*M*)-**1b** to stable (*P*)-**1a'** results from the thermal helix inversion of the motor. This inversion process and, as a consequence, the reverse color change (Figure 1 b) is slower at room temperature due to the high Gibbs energy of activation ($\Delta G^{0\ddagger} = 88 \text{ kJ mol}^{-1}$) of the helix inversion.^[11]

Conclusions

The use of molecular motor **1** as a chiral switchable dopant in LC host E7 makes it possible to generate colored LC films, the color of which can be adjusted by light- and heat-triggered isomerization of the motor. Due to the large magnitudes and opposite signs of the helical twisting powers of the stable and unstable forms of **1** in E7, all colors in the visible spectrum can be addressed in a fully reversible manner. At this point, the hypsochromic step is still rather slow relative to the bathochromic step. The use of a molecu-

lar motor with a faster thermal helix inversion^[11,13] could lead to reduced color-switching times, thus further improving the system. Studies along these lines are currently underway.

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