Unidirectional rotary motion in a liquid crystalline environment: Color tuning by a molecular motor

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Life could not exist without motion induced by a variety of molecular motors. The construction of artificial motors by chemical synthesis, which can power motions that lead to macroscopic detectable effects in a system, is a major endeavor in contemporary science. To move toward this goal, a host–guest system, composed of a nematic liquid crystal film doped with a chiral light-driven molecular motor, is assembled. Irradiation of the film results in unidirectional rotary motion of the molecular motor, which induces a motion of the mesogenic molecules leading to a molecular reorganization and, as a consequence, a change in the color of the film. In this way, by control of the rotary motion at the molecular level, color tuning over the entire visible spectrum is achieved. These findings demonstrate that a molecular motor can exert a visually observable macroscopic change in a material.

Inspired by nature’s nanomachinery, there is great current interest in the design of molecular systems that mimic motor functions and are capable of performing linear or rotary movement (1–4). Among the fascinating structures designed to induce mechanical motions are shuttles, muscles, ratches, pseudorotaxanes, and switches (5–12). Recently, the first examples of unidirectional rotary motors were reported (13, 14), and it was shown that the rate of the rotary motion in the light-driven motors could be tuned by structural modification (15). A major challenge is to use a molecular motor for a practical application by exerting a macroscopic change in system (16, 17). Such an application implies that the rotary motion at the molecular level should induce a mechanical effect in the system sufficiently large to allow easy detection by a change in macroscopic properties.

We report here a light-driven rotary motion in liquid crystalline (LC) films that induces a reorganization of the mesogenic molecules, as observed by visual inspection of the change in color of the LC film. Besides a potential information storage system with nondestructive read-out capabilities, these findings demonstrate the possibility of using the light-driven motor to tune the color gradation of an LC device over the entire visible spectrum by light irradiation.

After extensive studies on the thermal and photochemical isomerization processes of biphenanthrylidenes (18–21), we could demonstrate that the intrinsic chirality and dynamic properties associated with chiroptical molecular switches can be used to accomplish unidirectional rotary motion. With sterically overcrowded alkene [(3R,3’R)-(P,P)-trans-1,1’-2,2’-3,3’-4,4’-octahydro-3,3’-dimethyl-4,4’-biphenanthrylidenyl; 1a], where the two methyl substituents because steric effects adopt an energetically unfavorable axial orientation. Helix inversions of unstable (M,M)-cis-2b and unstable (M,M)-trans-1b release the energy in a unidirectional process to form the stable isomers (P,P)-trans-1a to (M,M)-cis-2b and (P,P)-cis-2a to (M,M)-trans-1b, where, by the nature of the process, in both cases the methyl substituents are forced to adopt an energetically unfavorable equatorial orientation. The direction of this rotation is controlled solely by the configuration at the stereogenic centers. This first example of a unidirectional light-driven molecular motor allows repetitive controlled 360° rotations.

In the development of advanced molecular machinery, retention of the photochemical properties when the molecular motor is incorporated in, for example, a polymeric or liquid crystalline matrix, organized on a surface, or becomes part of a supramolecular assembly, is an important issue. In the present study, we

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Abbreviations: LC, liquid crystalline; RT, room temperature; M15, 4-pentyl-4’-biphenylcarbonitrile.

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focus on using the light-driven motor to control the organization of an LC matrix and, in the reverse sense, employing the changes in an LC matrix to visualize rotary motion at the molecular level.

Photochemically tunable doped cholesteric liquid crystals are promising materials for LCD application (22, 23), and full-color control by adjusting the pitch of a cholesteric phase in a reversible manner by irradiation is particularly challenging (24–26). It is well known that the organization in the LC matrix is usually sensitive to the nature of (chiral) dopants present (27). Based on this property, a variety of photochromic compounds have been used to alter the alignment of LC phases upon irradiation (22, 23, 28, 29). It has been demonstrated that switching between positive and negative cholesteric phases could be accomplished by using chiroptical molecular switches (28–30). Cholesteric LC films show reflection at a specific wavelength (λ) dependent on the pitch (p), the angle of the incident light (α), and the average refractive index (n):

\[ \lambda(\alpha) = n \times p \times \cos \left[ \sin^{-1} \frac{\sin \alpha}{n} \right] \]

\[ = n \times \frac{1}{c \times \beta \times \cos \alpha} \times \cos \left[ \sin^{-1} \frac{\sin \alpha}{n} \right] \]

The pitch of a doped cholesteric phase is inversely proportional to the concentration (c), enantiomeric excess (ee), and helical twisting power (β) of the chiral dopant. The helical twisting power is an intrinsic property of any chiral dopant, and indicates how efficiently this molecule induces a chiral orientation in the LC material. When the pitch is in the range of the wavelength of visible light, a well defined, bright reflection and a distinct color are observed. Requirements for reversible light-induced color tuning in rewritable color-image formation are stability and reversibility, high helical twisting powers (β) to reach the appropriate pitch, and reflection in the visible spectrum—as well as sufficiently large changes in β-values upon irradiation.

Materials and Methods

Materials. 4-Pentyloxy-4’-biphenylcarbonitrile (M15) was obtained from Aldrich, Zwijndrecht, The Netherlands, and was used without prior purification. This compound shows nematic liquid crystalline behavior in the range of 48–67°C. Nematic liquid crystal E7, which is a mixture of different mesogenic compounds, was obtained from Merck, Darmstadt, Germany, and was used without prior purification. This mixture is designed to be liquid crystalline at room temperature (RT). Molecular motor (3R,3′R)-(P,P)-trans-1,1′,2′,2′,3′,3′,4,4′-octahydro-3,3′-dimethyl-4,4′-biphenanthrylidene 1a was prepared as reported (20). Enantiomerically pure (P,P)-trans-1a (P,P)-cis-2a and (M,M)-trans-1b were fully characterized and described (13, 20, 31, 32).

Alignment of LC Layers. For all measurements described here, aligned cholesteric phases were obtained in the following way. A glass surface (typically 6.25 cm²) was spin-coated with commercially available polyimide AL1051 (JSR, Leuven, Belgium). The coated samples were allowed to harden at 170°C in vacuum for 3 h. The surface then was linearly rubbed with a velvet cloth to induce a parallel-alignment in the LC samples. The liquid crystalline material doped with the appropriate amount of enantiomerically pure 1a was dissolved in toluene (typically, 1 ml of toluene was used per 5 mg of sample) and slowly poured onto the aligned surface. For the M15-doped material, the surface was heated to 50°C, whereas for the E7-doped material, RT was sufficient. After slow evaporation of the toluene at the appropriate temperature, an aligned LC film was obtained that was suitable for measurement of reflection wavelengths.

Measurement of Cholesteric Pitches and Reflection Wavelengths. Cholesteric pitches were determined with the Grandjean-Cano technique (33). For this purpose, the aligned sample was prepared as described above and covered with a plane-convex lens of known radius (Linos Components; Radiometer, The Netherlands). Examination of the samples through a polarization

**Table 1. Helical twisting powers (β-values) of three forms of the molecular motor (1a, 2a, and 1b) in two different liquid crystalline hosts (M15 and E7)**

<table>
<thead>
<tr>
<th>Host</th>
<th>(P,P)-trans-1a</th>
<th>(P,P)-cis-2a</th>
<th>(M,M)-trans-1b</th>
</tr>
</thead>
<tbody>
<tr>
<td>M15 (50°C)</td>
<td>+75</td>
<td>+8</td>
<td>-18</td>
</tr>
<tr>
<td>E7 (20°C)</td>
<td>+69</td>
<td>+12</td>
<td>-5*</td>
</tr>
</tbody>
</table>

*Value calculated from helical twisting power for mixtures of known composition.
microscope showed concentric rings whose relative radii could be correlated to the pitch of the material. The sign of the cholesteric phases was determined with a contact method (34), where mixing of the samples with a doped cholesteric liquid crystal of known negative screw sense, consisting of dopant ZLI-811 (Merck, Darmstadt, Germany) in the appropriate liquid crystalline host, was tested. Reflection measurements were performed on a Jasco J715 Spectrophotometer (Jasco, Maarssen, The Netherlands) equipped with a fluorescence extension (a photomultiplier perpendicular to the direction of the light). This spectrophotometer was adapted to hold LC-covered glass plates in such a way that both the incident light beam as well as the photomultiplier tube were at an angle of 45° to the surface. Actual color photographs of the aligned cholesteric structures were taken with a Minolta 404Si single-lens reflex camera perpendicular to the LC-covered surface.

Irradiation and Analysis. Irradiations were performed with a 180-W Oriel Hg-lamp adapted with a Pyrex filter to obtain light with a wavelength longer than 280 nm. Ratios of the different forms of the molecular motor were determined by using HPLC on a silica column (5 μm, 250 × 4.6 mm; Econosphere Silica) and pure n-heptane as eluent, where the three different forms that are observable at RT [(P,P)-trans-1a, (P,P)-cis-2a, and (M,M)trans-1b] are readily separated (tR [(M,M)-trans-1b] = 11.0 min; tR [(P,P)-trans-1a] = 11.5 min; tR [(P,P)-cis-2a] = 12.2 min) from each other and the LC materials which are eluted only when n-heptane/ethyl alcohol 95/5 is used as the eluent. The ratio of the three forms was checked at their isosbestic point at 305.9 nm [for (P,P)-trans-1a and (P,P)-cis-2a] and 333.2 nm [for (M,M)-trans-1b and (P,P)-cis-2a] by PDA detection with a Waters 996 Diode Array Detector.

Results and Discussion

First, the chiral dopant properties and the helical twisting power of the motor were examined. The different chiral forms observed during a 360° rotation cycle are shown in Scheme 1. Doping of nematic 4-pentyloxy-4′-biphenylcarbonitrile (M15) with only 3.4 weight % of enantiomerically pure (3R,3′R)-(P,P)-trans-1a resulted in a stable cholesteric phase with a pitch of 390 nm. A high helical twisting power (β = +75 μm⁻¹), as determined by the Grandjean Cano technique (33), was found for (3R,3′R)-(P,P)-trans-1a. For comparison, the β-values for the stable cis-isomer (3R,3′R)-(P,P)-cis-2a and the unstable trans-isomer (3R,3′R)-
(M,M)-trans-1b in M15 were measured. Furthermore, the β-values of the three stereoisomers were determined in E7, an LC mixture which is nematic at RT. No β-value for the unstable (3R,3'R)-(M,M)-cis-2b could be determined because of the fast helix inversion of this compound forming stable (3R,3'R)-(P,P)-cis-2a at the appropriate temperatures. From the data given in Table 1, it is evident that (P,P)-trans-1a shows a high positive β-value, and a large decrease in helical twisting power is found going to (P,P)-cis-2a and (M,M)-trans-1b. It also should be noted that (P,P)-cis-2a shows positive β-values (right-handed cholesteric), and (M,M)-trans-1b shows negative β-values (left-handed cholesteric).

Although the light-driven motor operates efficiently in solution, the unstable (3R,3'R)-(M,M)-cis-2b could be determined because of the fast helix inversion of this compound forming stable (3R,3'R)-(P,P)-cis-2a at the appropriate temperatures. From the data given in Table 1, it is evident that (P,P)-trans-1a shows a high positive β-value, and a large decrease in helical twisting power is found going to (P,P)-cis-2a and (M,M)-trans-1b. It also should be noted that (P,P)-cis-2a shows positive β-values (right-handed cholesteric), and (M,M)-trans-1b shows negative β-values (left-handed cholesteric).

Next, the LC film, now containing (M,M)-trans-1b, was heated at 60°C to allow the thermal helix inversion of unstable (M,M)-trans-1b to proceed to (P,P)-trans-1a. HPLC analysis showed that unstable (M,M)-trans-1b was quantitatively and stereoselectively converted into stable (P,P)-trans-1a in the LC matrix. This step completes the four-step clockwise rotation, demonstrating that a unidirectional rotary process is possible in an LC matrix. CD analysis of the isomers confirmed the stereochemical change during the rotary cycle.

Conclusions

In conclusion, we have shown that unidirectional rotary motion can be performed in an LC matrix. Furthermore, the light-driven motion of the dopant induces the motion of a large ensemble of rod-like molecules during the reorganization in the LC film, which allows direct visual observation of the rotary motion. The high helical twisting power of (P,P)-trans-1a in combination with the large change in β going to the other stages makes it possible that the reflection wavelength can be tuned readily throughout the entire visible spectrum simply by changing the irradiation time. Changing light intensity or irradiation wavelength would have a similar effect. These findings not only demonstrate that a macroscopic effect, i.e., a change of the physical properties of a material (in the present case, an LC film), can be induced by a rotary molecular motor, but also that color pixels in an LC film can be generated by using this supramolecular approach. The mechanism of the pitch increase in the LC phase and, in particular, the intriguing question of whether the molecular motor indeed drives the unidirectional unwinding of the helical packing of several molecules in the LC matrix merits further study.


