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Chemical Communications, 24: 3609-3611

2009-06-28

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article (author version)

CC24_3609-3611.pdf
Reversibly tunable helicity induction and inversion in liquid crystal self-assembly by a planar chiroptic trigger molecule

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Received (in XXX, XXX) Xth XXXXXXXXX 200X. Accepted Xth XXXXXXXXX 200X

First published on the web Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

Reversible control of the helical pitch length and inversion of its helical handedness in an induced cholesteric liquid crystal phase was accomplished via a combination of photochemical and thermal isomerizations of a planar chiral azobenzenophane molecule.

Controlling helicity induction and its inversion in artificial systems at different hierarchical levels of molecular self-assembly by external stimuli such as chiral dopants, temperature and light offers potential applications in asymmetric synthesis, sensing, and memory devices. Chiral liquid crystal (LC) molecules are well known to self-assemble into many technologically important helical phase structures. The most well known LC phase having helical structure is cholesteric (N*), in which the average direction of molecular axes rotates around a helical axis. Cholesteric phase reflect selectively the circularly polarized fraction of incident light satisfying the Bragg condition, $\lambda = nP$, where $\lambda$, $n$ and $P$ are wavelength, mean refractive index and helical pitch, respectively. Therefore, when its helical pitch ($P$) is comparable with the wavelengths of visible light, we see reflection colors from the cholesteric LC phase. More interestingly the helical pitch length can be designed to respond to various external perturbations such as dopants, temperature, light and electric fields to reversibly tune the reflected colors for various applications in modern color information technology. Although, enantiomers of a chiral dopant are known to induce an equal but opposite twist in the cholesteric phase, a reversible switching of the helical handedness by light and temperature proved to be a challenging task.

A chiral photoresponsive dopant can act as both a chiral agent to induce a chiral nematic phase in a nematic liquid crystal and a photoresponsive moiety to control the helical pitch through photo-isomerization. Considerable progress have been made towards the photo modulation of the helical pitch length by the design of dopants incorporating photoresponsive moieties such as azobenzenes, fulgides, diarylethenes, spiropyrans, and overcrowded alkenes with point, axial, and helical chirality. However, chiral switchable dopants with ability to induce cholesteric helix of opposite sign for both switch states remains rarely known. Over the past decade, we have been exploring the strategies to address the reversible cholesteric reflection color control over the entire visible range for applications in optically rewritable memory devices. Recently, we reported the first example of a photoresponsive planar chiral dopant in the form of a monocyclic azophane and successfully achieved a fast photon mode reversible full-range color control in induced cholesterics. Here we report our success in reversibly controlling the helical pitch length as well as the handedness of the induced helix by photochemical and thermal isomerizations of a planar chiral bicyclic azobenzenophane (1) in host nematic LCs.

Target molecule was synthesized as pure trans isomer of the racemic compound $E,E$-1 and the structure was fully characterized by NMR and X-ray crystallographic analysis. The restricted “flip-flop” of the 2,2-diphenylpropane unit through the cyclophane cavity (Fig. 1) impart an element of planar chirality to the molecule. Chiral HPLC analysis confirmed the existence of a pair of enantiomers. We resolved racemic $E,E$-1 through preparative HPLC using a chiral column. The enantiomer that eluted first, which we assigned as $S,E,E$-1, exhibited CD bands at 230, 350, and 455 nm with $\Delta\varepsilon$ of +78, +70 and ~65 M$^{-1}$ cm$^{-1}$ respectively. As expected, the second eluted enantiomer $R,E,E$-1 shows a complete mirror image CD spectrum of its enantiomer (Fig. 2). In solution, $E,E$-1 undergoes efficient cis-trans isomerizations by UV and visible light irradiations (Fig. 3). Absorption spectra exhibit distinct bands for $\pi-\pi^*$ and $n-\pi^*$
Next we investigated the potential of \((R)E,E\)-1 and \((S)E,E\)-1 as chiral transfer agents in three structurally different\textsuperscript{15} commercially available host nematic liquid crystals (NLCs) namely ZLI-1132, DON-103 and 5-CB. As expected, all the LC mixtures induced a chiral N phase which was evidenced as a fingerprint texture\textsuperscript{10} under polarized optical microscope. When a chiral solute is dissolved in nematic liquid crystal at the limit of low concentration, the induced pitch \(P\) is correlated with the weight concentration \(C_w\) of the dopant (weight of dopant / weight of host NLC) and its enantiomeric purity \(r\) according to the equation \(P^{-1} = \beta C_w r\). The proportionality constant \(\beta\) is referred to as the helical twisting power (HTP). The induced helical pitch and its thermal and photoresponsive behavior was measured using Cano wedge cells.\textsuperscript{16} The corresponding change in HTP values were calculated based on above mentioned equation and the results are summarized in Table 1.

Table 1. Helical twisting power (\(\beta\mu m^{-1}\)) of dopants in different NLC hosts as determined by Cano’s wedge method and the observed change in values by irradiation.\textsuperscript{10}

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Host</th>
<th>(\beta) ((\mu m^{-1}))</th>
<th>(\Delta P) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>((R)E,E)-1</td>
<td>NLC</td>
<td>Initial PSS\textsubscript{UV} PSS\textsubscript{vis}</td>
<td>PSS\textsubscript{vis}</td>
</tr>
<tr>
<td>5CB</td>
<td>-6</td>
<td>+32</td>
<td>+26</td>
</tr>
<tr>
<td>ZLI-1132</td>
<td>-7</td>
<td>+28</td>
<td>+23</td>
</tr>
<tr>
<td>DON-103</td>
<td>+5</td>
<td>+37</td>
<td>+28</td>
</tr>
<tr>
<td>((S)E,E)-1</td>
<td>5CB</td>
<td>-6</td>
<td>-26</td>
</tr>
<tr>
<td>ZLI-1132</td>
<td>+7</td>
<td>-28</td>
<td>-23</td>
</tr>
<tr>
<td>DON-103</td>
<td>-5</td>
<td>-37</td>
<td>-28</td>
</tr>
</tbody>
</table>

\textsuperscript{10} Positive and negative values represent right-and left-handed helical twists, respectively. \textsuperscript{11} Percent change in \(P\) observed from initial to PSS\textsubscript{vis}.

Both dopants in its all trans isomer configuration \(i.e., (R)E,E\)-1 and \((S)E,E\)-1 show very low HTP values in all the three host NLCs. The helical sense of the induced N* phase was determined by both contact as well as color shift method.\textsuperscript{15} Chiral dopant \((R)E,E\)-1 in 5CB and ZLI-1132 induced a left-handed helix, while a right-handed helix was obtained from its enantiomer \((S)E,E\)-1. Interestingly, an opposite helix sense was induced by \((R)E,E\)-1 and \((S)E,E\)-1 in DON-103 i.e., a right-handed helix by \((R)E,E\)-1 and a left-handed helix by \((S)E,E\)-1. This could be explained based on the difference in intermolecular associations between dopants and the hosts; 5CB and ZLI-1132 have rigid biaryl moieties and high longitudinal dipole, whereas DON-103 posses flexible ester linkage and transverse dipole. In the next step we investigated the effect of isomerization of dopants on the pitch values and helix handedness. Photoinduced variations in HTP values and the pitch were directly observed as change in distance between the Cano lines when sample in a wedge cell was observed with a polarized optical microscope under UV or visible light illumination (Fig.4). During the process of UV irradiation of LC mixtures containing 1 wt% of \((R)E,E\)-1 and \((S)E,E\)-1 in 5CB and ZLI-1132, to begin with Cano lines disappeared completely (with in 20 s of irradiation) before reappearing again on continuing the irradiation to attain the PSS\textsubscript{vis} in about 90 s. The distance between the lines were considerably shortened at PSS\textsubscript{vis} pointing to an increase in the HTP and thus shortening of the helical pitch length due to \(trans\text{-}cis\) isomerization. More interestingly, we found that helicity of the induced N* phase at PSS\textsubscript{vis} to be opposite to that of the initial state in all the four LC mixtures.
Observation of N phase due to destabilization of the initially induced helical structures by **trans-cis** photo-isomerization prior to regeneration of cholesteric helix supported the argument of helical switching. An increase in distance between the Cano lines were observed upon visible light irradiation of the sample in **PSS\text{UV}** induced N* phase due to the reverse process. However, the Cano lines never disappeared on the course to the **PSS\text{Vis}** state and did not result in any change in sign of the cholesteric helicity. This was further confirmed by observing a change in sign of the cholesteric helicity even by visible light irradiation of the initial sample. The effective change in HTP values by alternate visible and UV irradiations were calculated to be about 40% effective change in the induced pitch by alternate irradiations were calculated to 23% and 22% for 5CB and ZLI-1132 LC mixtures respectively. Helicity reverted to the initial state by allowing the LC mixture to relax back to the thermodynamically favourable **trans** form in the dark in about 12 hours. Although the presence of two azobenzene moieties make the PSS compositions complex, it is possible to calculate the HTP of **E,Z** and **Z,Z** isomers using the known isomeric compositions and values of HTP at PS\text{SUV}s and pure **E,E** isomer. For example, we obtained HTP values for (R)\text{E,E-1} and (R)\text{Z,Z-1} in 5CB as +57 and +22 respectively. These observations clearly demonstrate that photoisomerized **E,Z** and **Z,Z** isomers induce an opposite cholesteric helix to that of **E,E** isomer in 5CB and ZLI-1132 NLC hosts. On the contrary, (R)\text{E,E-1} and (S)\text{E,E-1} in DON-103 did not show any switching of helicity by photoisomerization. LC mixtures with these dopants shown significant increase in HTP values with **E,E** to **E,Z** and **Z,Z** photoisomerization. The process was reversed on illumination with visible light and about 40% effective change in the induced pitch by alternate irradiations was achieved.

In summary, bicyclic azophanes with planar chirality was employed as photochromic dopants to induce helicity in N host LCs. We could reversibly control the helical pitch length and more importantly achieve a change in sign of helicity by external light stimuli. A better understanding of solvent-solute interactions on the chirality transfer is required to explain the observed NLC host dependent helicity switching. More examples of planar chiral photoresponsive molecules are under investigation for applications in light driven artificial systems.

This work was supported by a grant-in-aid for science research in a priority area "New Frontiers in Photochromism (No. 471)" from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan.

### Notes and references

- See the supporting information.