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

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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 hierarchial levels of molecular self-assembly by external stimuli such as chiral dopants,[1] temperature[2] and light[3] offers potential applications in assymetric synthesis,[4] sensing,[5] and memory devices.[6] Chiral liquid crystal (LC)molecules are well known to self-assemble into many technologically important helical phase structures.[7] 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 λ, n and P are wavelength, mean refractive index and helical pich, 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 reveisbly tune the reflected colors for various applications in modern color information technology.[8] 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 photo-responsive moieties such as azobenzenes, fulgides, diarylethenes, spiropyrans, and overcrowded alkenes with point, axial, and helical chirality.[9] However, chiral switchable dopants with ability to induce cholesteric helix of opposite sign for both switch states remains rarely known.[10,11]

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 rewrittable memory devices.[8, 12] 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.[13] 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.
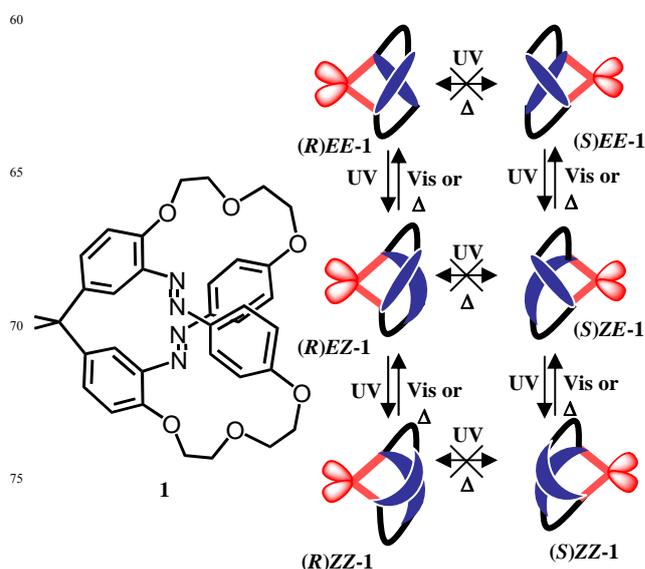
Fig.1 Structure of planar chiral bicyclic azobenzenophane (**1**) and the schematic representation of photochemical and thermal processes taking place in its *R* and *S* enantiomers. Blue structure in the scheme represent photochromic azobenzene unit.

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.[14] 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 existance 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 π-π* and n- π*
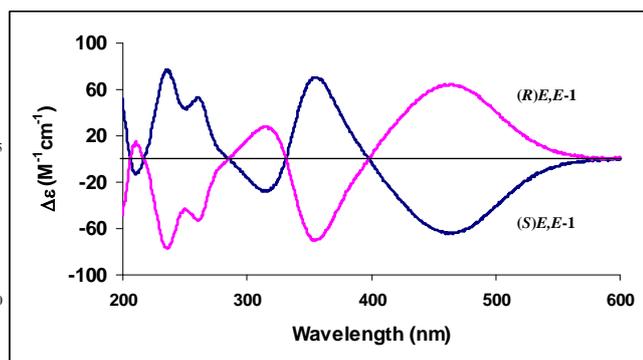
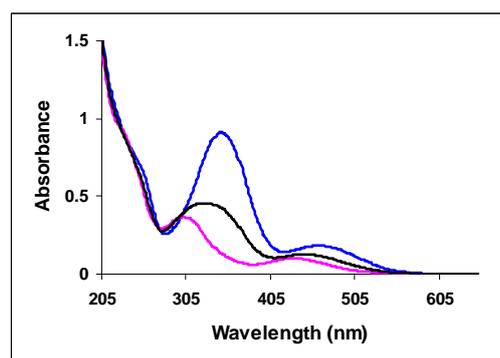Fig.2 CD spectra of enantiomers of **1**; **(S)E,E-1** (blue line) and **(R)E,E-1** (red line) in CH₃CN.

Fig.3 Absorption spectral change of **E,E-1** in acetonitrile upon irradiation at room temperature: (a) blue line, initial state before irradiation; (b) red line, photostationary state (PSS) after irradiation at 365 nm; and (c) black line, PSS after irradiation at 436 nm.

transitions of the azochromophore. Upon UV irradiation (λ_{max} = 365 nm) due to photochemical *trans* (*E,E*-1) to *cis* (*E,Z*-1 and *Z,Z*-1) isomerization, there is a gradual decrease seen in the π-π* transition bands in the absorption spectra with concomitant increase in the n-π* band around 450 nm. Photostationary state (PSS) was reached after UV irradiation for about 60 s. We determined the ratio of *trans*:*cis* isomers in the PSS$_{UV}$ as 87% (*Z,Z*-1), 12% (*E,Z*-1) and 1% (*E,E*-1) by HPLC analysis. On visible light irradiation (λ_{max} = 436 nm) reverse absorption changes occurred and a PSS$_{vis}$ was obtained in about 90 s. The relative concentrations of the *E,E*, *E,Z* and *Z,Z* isomers in the PSS$_{vis}$ were 23%, 47% and 30% respectively. By chiral HPLC analysis we confirmed that racemization between the enantiomers does not occur either thermally or photo-chemically. In other words, the size of the cyclophane cavity formed for *E,E*, and *Z,Z* isomers are shallow enough to prevent the racemization. On the contrary, its higher homologue obtained by increasing the chain length of ethylene glycol unit resulted in photo-induced racemization through its *Z,Z* isomer.[14] Fig.1 summarizes the isomerization characteristics of **(S)E,E-1** and **(R)E,E-1** enantiomers in solution, highlighting their photochemically and thermally reversible isomerization to **(S)E,Z-1**, **(S)Z,Z-1** and **(R)E,Z-1**, **(R)Z,Z-1** respectively without undergoing any racemization.

Next we investigated the potential of **(R)E,E-1** and **(S)E,E-1** as chiral transfer agents in three structurally different[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[16] 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 putiry *r* according to the equation $P^{-1} = \beta C_w r$. The proportionality constant β 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.[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[a].

Dopant	Host NLC	β (μm^{-1})			$\triangle\beta$ [%][b]
		Initial	PSS$_{uv}$	PSS$_{vis}$	
(R)E,E-1	5CB	− 6	+ 32	+ 26	633
	ZLI-1132	− 7	+ 28	+ 23	500
	DON-103	+ 5	+ 37	+ 28	640
(S)E,E-1	5CB	+ 6	− 32	− 26	633
	ZLI-1132	+ 7	− 28	− 23	500
	DON-103	− 5	− 37	− 28	640

[a] Positive and negative values represent right-and left-handed helical twists, respectively. [b] Percent change in β observed from initial to PSS$_{UV}$.

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.[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 transeverse 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). Duing 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$_{UV}$ in about 90 s. The distance between the lines were considerably shortened at PSS$_{UV}$ pointing to an increase in the HTP and thus shortening of the helical pitch length due to *trans-cis* isomerization. More interestingly, we found that helicity of the induced N* phase at PSS$_{UV}$ to be opposite to that of the initial state in all the four LC mixtures.
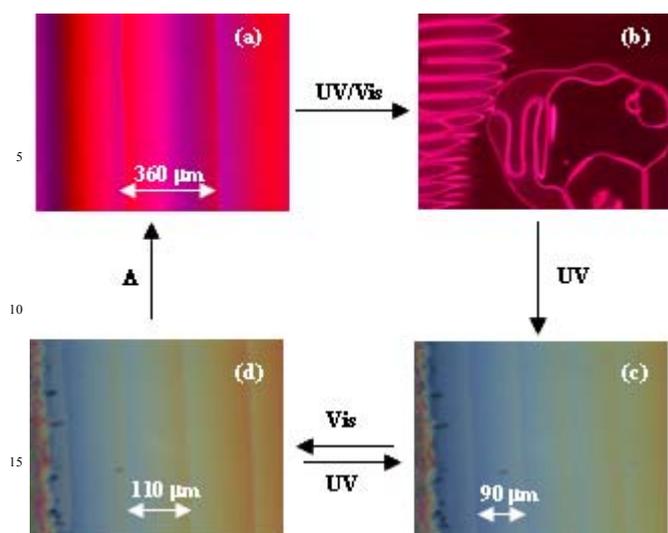
Fig.4 Polarized optical photomicrographs of 1 wt% of (**R**)**E,E-1** dissolved in ZLI-1132 at RT: Reversible change occurring in pitch by irradiation of sample in a wedge type cell; (a) before irradiation, (b) N phase obtained by exposure of sample to UV or Vis irradiation, (c) PSS$_{UV}$, (d) PSS$_{VIS}$.

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 arguement of helical switching. An increase in distance between the Cano lines were observed upon visible light irradiation of the sample in PSS$_{UV}$ induced N* phase due to the reverse process. However, the Cano lines never disappeared on the course to the PSS$_{Vis}$ 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 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 PSSs and pure *E,E* isomer. For example, we obtained HTP values for (**R**)**E,Z-1** and (**R**)**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**)**E,E-1** and (**S**)**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 arificial systems.

Notes and references

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