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A helical naphthopyran dopant for photoresponsive cholesteric liquid crystals†

Yuna Kim, Michel Frigoli, Nicolas Vanthuyne and Nobuyuki Tamaoki*
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The first photoresponsive cholesteric liquid crystal comprising a photoisomerizable helical naphthopyran derivative dopant and a nematic liquid crystal is reported. An unprecedented helical twisting power switching ratio of over 90% allowed us to demonstrate multi-cycle rotational motion of micro-objects by UV light irradiation.

Photochromic compounds have been widely applied to supramolecular systems in recent years, acting as phototriggers that undergo photoisomerization which induce dynamic macroscopic reorganization of superstructures by light irradiation.1–3 In the case of liquid crystals, a chiral photochromophore is dissolved into an achiral nematic liquid crystal (NLC), and its molecular chirality can be transferred to the NLC medium resulting in a photo-responsive nematic chiral (N* or cholesteric) liquid crystal phase.4–6 Those photo-responsive cholesteric liquid crystals (CLCs) have been extensively utilized for light-driven polarizers, reflectors, displays, tunable solid state lasers, and molecular motor applications.6–14

Among the dopants for CLCs, helicene-like molecules are well known to provide amplified chirality transfer to the nematic host because of their intrinsic helical conformation.15,16 However, photoisomerizable helicene derivatives are rather unexplored as photoresponsive dopants compared to photochemically reversible P-type molecules, such as diarylenes and azobenzenes.1–6

Recently, Frigoli et al. reported on the novel photochromism of helical naphthopyrans overcoming fast thermal relaxation,17,18 and we anticipated that its reversible conformational change could provide efficient superstructural manipulation of CLCs. There has been a report on a non-chiral naphthopyran derivative which induces liquid crystallinity in the nematic LC host by photoisomerization,19 whereas, to the best of our knowledge, the formation of a cholesteric superstructure and its manipulation have never been exploited based on the photoswitching of naphthopyran derivatives introduced as chiral dopants.

We describe here the first example of a naphthopyran derivative which can be a promising candidate for photocontrol of macroscopic helical superstructures exhibiting a reversible photoisomerization process accompanying a large conformational change: unprecedented large photoswitching of helical twisting power of over 90% and the most efficient induction of macroscopic rotational motion of micro-sized objects reported so far (a rotation angle of 1150° at 0.2 wt%) to the best of our knowledge, on the surface of cholesteric LC films.

Synthesis of a helical naphthopyran derivative, CHR-Hexyl (10-hexyl-3,3-diphenyl-[3H]-benzo[5,6]phenanthro[4,3-f]chromene), is described elsewhere,18 and its molecular structure and the photoisomerization process are described in Fig. 1. Photoisomerization was conducted using 365 nm (9.1 mW cm−2) and 510 nm (26.5 mW cm−2) LED light sources for both solutions and CLCs containing CHR-Hexyl. Upon UV irradiation, the closed ring form (CF) gives open metastable photoproduct(s) with the structure of zquinone allides, which are generally coloured, owing to improved electronic delocalisation compared with the closed form. The transoid-trans (TT) isomer is more thermodynamically stable than the transoid-cis (TC) one and is the major photoproduct (up to 92% conversion ratio from CF to TT) at the photostationary state upon continuous irradiation.18 Coloured forms can reconvert to the starting material both thermally and upon visible irradiation. Detailed photochemical characteristics of CHR-Hexyl are described in ref. 18.
The separation of the enantiomers was performed by chiral HPLC using a semi-preparative (S,S)-Whelk-O1 column (Fig. S1, ESI†). The analytical resolution and evaluation of chiroptical properties were performed by chiral HPLC using a Chiralpak IA column (see Fig. S2a–g, ESI†) and circular dichroism (CD) spectroscopy. The two enantiomers M and P of CHR-Hexyl have different retention times (Rₜ) of 16.8 and 16.0 min, respectively, using dichloromethane and hexane (1:2) as eluent. Upon 365 nm light irradiation, the appearance of new peaks (Rₜ = 22.5 and 31.0 min) is assignable to the TT forms of enantiomers M and P, respectively. Subsequent thermal relaxation resulted in the recovery of the original peaks of closed ring forms of two enantiomers, and we could confirm almost no trace of racemization both after the ring opening photoisomerization and the subsequent thermal relaxation back to CF.

Chiroptical properties of the two enantiomers of CHR-Hexyl were investigated using circular dichroism (CD) spectroscopic analyses at room temperature. Fig. 2 shows CD spectra recorded for the enantiomers M and P in toluene (2.5 × 10⁻⁵ M). They show mirror image features before and after photoirradiation. The CD spectrum of M shows positive bands at 286 nm, 302 nm and 420 nm, and a strong negative band at 333 nm before UV irradiation. Upon 365 nm LED light source irradiation for the initial 30 seconds, it exhibited significant spectral change. The positive bands at 286 nm and 302 nm merged with the positive band at 299 nm with increased intensity which is consistent with the UV-Vis absorption spectral change,¹⁸ and the negative band at 333 nm shifted to 362 nm with two shoulder bands at 343 and 375 nm with decreased intensity. The small band at 420 nm disappeared and one negative and one positive band in the visible region at 452 nm and 515 nm, respectively, emerged reflecting the presence of colored forms.

Comparing the spectra between 30 seconds and 1 minute UV irradiation, no distinctive change was observed, while subsequent UV light irradiation for more than 5 minutes resulted in continuous decreasing of the bands’ intensities. Enantiomer P also showed consistent phenomena which shows mirror features with respect to enantiomer M. The clear difference between 0 and 30 second irradiation followed by the subtle transition to 1 minute is attributable to the transition from CF to TT. Consecutive irradiation resulted in TT formation leading to a reduction of its helicity which was apparently observed from the decreasing of the band intensities. After 15 minutes of UV irradiation, thermal back reaction from TT to CF was monitored over 500 hours (Fig. S3, ESI†). Slight band recovery (increment) at 333 nm, and re-splitting of the 299 nm band to 286 nm and 302 nm were observed which could be ascribed to the very slow return to the initial CF. CHR-Hexyl exhibited much slower thermal back transition in toluene compared to that in a mixture of hexane and dichloromethane which was observed from absorption spectra and the chiral HPLC chromatogram (Fig. S2, ESI†).

The difference in lifetime of TC and TT depending on the solvent nature has been discussed in a previous report.¹⁸ Based on the chiroptical properties, we examined the chirality transfer characteristics of CHR-Hexyl in a nematic liquid crystal medium at room temperature. The chiral nematic liquid crystal composite was prepared by dissolving one of the enantiomers of CHR-Hexyl M or P and the host liquid crystal such as 4-phenyl-4′-cyanobiphenyl (5CB), JC-1014XX, and E-7. The homogeneous CLC mixture was injected into a wedge cell by capillary force at room temperature, and clear Cano’s lines²⁰ were observed under a polarizing optical microscope, which represents the formation of cholesteric orientation of the molecules (Fig. 3 and Fig. S4, ESI†).

Wedge cells filled with the chiral LC mixture containing M showed a color shift towards the thinner region of the wedge upon turning the analyzer (located on the opposite side of the light source with respect to the cell) in a clockwise direction.

Fig. 2 CD spectra of the toluene solution (2.5 × 10⁻⁵ M) of two enantiomers M (solid line) and P (dashed line) upon UV light irradiation.

Fig. 3 Cano wedge cell images with Cano lines (white scale bar: 500 μm) obtained from CLC mixtures containing 1 wt% of CHR-Hexyl and JC-1014XX (a) initial, P = 3.5 μm and (b) PSS₃₆₅₅₀, P = 50 μm), 1 wt% of CHR-Hexyl and E7 (c) initial, P = 3.8 μm and (d) PSS₃₆₅₅₀, P = 55.6 μm), and 12 wt% of CHR-Hexyl and 5CB (e) initial, P = 4.2 μm and (f) PSS₃₆₅₅₀, P = 55 μm).
which indicates that the helix is left-handed or bears a negative (−) helical twist. On the other hand, wedge cells with P showed right-handed or (+) twist sense which is opposite to that of M.

The ability of a chiral molecule to induce a helical structure in CLC can be quantified as the helical twisting power (HTP, β) and expressed by the equation $\beta = (PC)^{-1}$, where C is the concentration of the chiral dopant, and P is the pitch that corresponds to the distance over which the director of molecules undergoes one full turn. $^2,3$ The HTP and the resultant helical pitch highly depend on the conformational change of the chiral dopant. $^3,5$ The helical pitch length was determined by Cano’s wedge method (see the ESI†), $^{20}$ and its photoinduced variations were evaluated upon UV (365 nm) illumination to the wedge cell which resulted in surprisingly huge widening of the gap between Cano lines for all CLCs as shown in Fig. 3. It took over 1 minute to initiate the lengthening of the distance between Cano’s lines by UV light irradiation. This delayed photoresponse would be attributed to the transition between CF and thermodynamically less stable TC-rich states. Based on the obtained helical pitch lengths of CLCs containing CHR-Hexyl (M) and NLC hosts such as JC-1014XX, E7 and 5CB (Fig. 3), each HTP value before (initial) and after UV light irradiation (PSS$_{365\text{nm}}$), and the switching ratio $(|\Delta \beta|/\beta_{\text{in}})$ were calculated and are described in Table 1.

Table 1  HTP switching of CHR-Hexyl (M) in NLC hosts$^a$ upon UV light irradiation

| NLC         | HTP (β)$_b$ μm$^{-1}$ | PSS$_{365\text{nm}}$ | $|\Delta \beta|/|\beta_{\text{in}}|\times100$ (%) |
|-------------|----------------------|----------------------|-----------------------------------------------|
| JC-1014XX   | −28.5                | −2.0                 | 93.0                                          |
| E7          | −26.4                | −1.8                 | 93.2                                          |
| 5CB         | −20.0                | −1.5                 | 92.5                                          |

$^a$ Determined using Cano’s wedge method and the change in HTP under each photoirradiation condition. $^b$ Percentage change in HTP observed between the initial state and PSS$_{365\text{nm}}$ [($|\beta_{\text{fin}}| - |\beta_{\text{in}}|$)/$|\beta_{\text{in}}|$].

The doped liquid crystalline mixture with CHR-Hexyl (M) enantiomer was drop-cast onto a glass substrate coated with a unidirectionally rubbed polyimide alignment film, $^{12,22}$ and was then observed under an optical microscope equipped with a polarizer at room temperature. Clear fingerprint textures were observed, which is a direct consequence of the cholesteric geometry, by aligning the axis of the cholesteric helix parallel to the substrate at the interface between the liquid crystal and air. The line width from a polygonal fingerprint texture corresponds to half of the cholesteric pitch (P) length. $^{22}$ After verifying the formation of polygonal textures, we freckled glass rods (average length: 25 μm; average diameter: 5 μm) onto the film surface and then irradiated the films with light of 365 nm. Fingerprint textures were dynamically reorganized and relaxed, and finally almost disappeared by attaining the TT-rich state of the chiral dopants accompanying the anti-clockwise rotation of the glass rods as shown in Fig. 4 from (a) to (h).

Fig. 5a depicts the rotational angle change depending on the UV irradiation time. Rotation became fast when it passed the threshold at around 40 s, presumably exceeding the boundary irradiation dose of transition from CF–TC to the TT form. It decreased as irradiation continued and eventually stopped due to attainment of the photostationary state of the dopant. Almost 3 full cycles ($115^\circ$) were achieved with irradiation for 5 minutes. As a subtle angular change was observed afterwards, the UV light source was removed and the thermal back reaction-induced mechanical motion was monitored at room temperature. Dissipated fingerprint texture gradually reoccurred accompanying the clockwise rotational motion of glass rods (Fig. 4 from (i) to (l)).
advantageous to provide an exceptionally efficient molecular machinery system. It is ascribed to the transition of the rigid helical geometry (CF) to loosened and elongated helicity (TT) which dramatically reduces chirality transfer of CHR-Hexyl resulting in a large HTP switching ratio of over 90%. Moreover, the high thermal stability of the TT form after UV irradiation resulted in very slow backward rotation, which has never been demonstrated so far, and possibly led to the much precise control including the bistable memory of rotation angles.

In conclusion, we demonstrated photoresponsive CLCs comprising a photoisomerizable naphthopyran dopant for the first time exhibiting both dynamic helical reorganization performance and unique high thermal stability by CF–TT isomerization. It is highly expected that the novel system can be exploited to provide bistable phototunability of mechanical work.

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Notes and references