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Supramolecular Chemistry

Azoarenes with Opposite Chiral Configurations: Light-Driven Reversible Handedness Inversion in Self-Organized Helical Superstructures**

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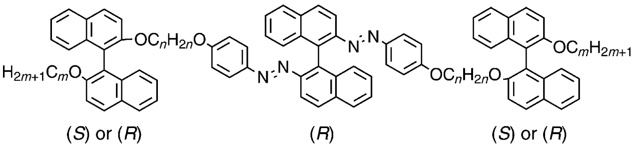
Dedicated to Professor Armin de Meijere on the occasion of his 74th birthday

Stimuli-directing self-organized supramolecular architectures with tailored functional groups have proven important for the design of intelligent molecular devices.[1] Light-driven induction of helicity and inversion of handedness in self-organized helical superstructures, that is, cholesteric liquid crystals (CLCs) have the unique property of selective reflection of circularly polarized light (CPL) and the advantages of remote, spatial, and temporal controllability. Such systems might be achieved by doping photoresponsive chiral molecules into an achiral nematic liquid-crystal (LC) host to self-organize into an optically tunable helical superstructure.[2] However, to date, the photoresponsive chiral dopants capable of inducing light-driven handedness inversions in self-organized helical superstructures mainly depend on chance, that is, it is not predictable for a photoresponsive chiral molecule to induce handedness inversion driven by light. Compared with the intensive studies on the optically tunable helical superstructures without handedness inversion,[3,4] developing novel photoresponsive chiral dopants capable of inducing light-driven handedness inversion in a self-organized helical superstructure, that is, reversibly tuning the handedness between left-handed and right-handed, still remains a challenging task.[5] Nevertheless, controlling the chirality with helix inversion in a helical superstructure is associated with the handedness inversion of CPL that it reflects, holding great potential for the development of smart stimuli-responsive materials for future applications, especially in the areas in which CPL is involved.[6,7]

A few examples of handedness inversion in self-organized helical superstructures have been demonstrated with photoresponsive chiral dopants.[8–12] These systems require that the dopants either reverse their intrinsic chirality (e.g., sterically overcrowded alkenes)[8] or switch between two isomers with dramatically different conformations (e.g., *transoid* and *cisoid* forms of binaphthyls) that can promote the helix inversion.[9,10,12] Their disadvantages include low helical twisting powers (HTPs) of dopants,[11,12] the requirement of specific LC hosts,[8,10,12] or very delicate syntheses.[8,9] More importantly, it is difficult to predict which system will induce helix inversion because of the subtle interplay of contributions from the molecular conformation change upon light irradiation and the dopant–host interactions. Rational design of photoresponsive molecules for handedness inversion would be of great interest and would significantly broaden their applications. Herein, we report a design strategy based on the chiral conflict and equilibrium shifting between multiple chiral moieties in a single molecule. A series of azoarene molecules (*S*,*R*,*S*)-**1a–c**, bearing axially chiral binaphthyl units of opposite chiral configurations (Figure 1), were synthesized, and they were found to induce the handedness inversion in different LC hosts upon light irradiation with moderate to high HTPs (Figure 2), where the chirality of each moiety does not need to be reversed. An azoarene comprising binapthyls with the same configuration, (*R*,*R*,*R*)-**1d**, was also prepared for comparison.



(*S*,*R*,*S*)-**1a** $m = 18, n = 11$; (*S*,*R*,*S*)-**1b** $m = 8, n = 6$
(*S*,*R*,*S*)-**1c** $m = 8, n = 3$; (*R*,*R*,*R*)-**1d** $m = 18, n = 11$

Figure 1. Molecular formulas of chiral azoarene dopants.

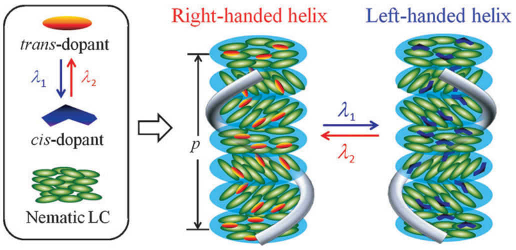


Figure 2. Schematic illustration of handedness inversion of a self-organized helical superstructure induced by a chiral azoarene dopant.

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The dihedral angle (θ) of two naphthyl rings in binaphthyl derivatives plays a role in their induction of helicity.[13] 2,2′-Disubstituted binaphthyl derivatives normally exhibit *transoid* conformations ($\theta > 90^\circ$) and the *R* configuration can induce the cholesteric phase with right handedness, while the *S* configuration results in left handedness.[14] Thus, incorporating multiple chiral binaphthyls into a single molecule functionalized with photoresponsive groups could be a novel route for not only generating materials capable of helix inversion but also probing the fundamental interactions of these molecules with anisotropic hosts. Hence, an axially chiral azoarene unit with *R* configuration was selected as the central scaffold owing to its high HTP in our previous research,[4b–d] and was laterally linked with two binaphthyl units with either an *S* or *R* configuration. The helicity induction of these compounds is determined by contributions from all three chiral moieties. If we could modulate the equilibrium between the opposite chirality at different states, that is, right-handed (*R*-binaphthyl) versus left-handed (*S*-binaphthyl), it is quite possible that the handedness could be inverted upon light irradiation. To this end, four compounds (*S*,*R*,*S*)-**1a**–**c** and (*R*,*R*,*R*)-**1d**, were prepared from commercially available starting materials with good yields (Supporting Information, Scheme S1).

The photoisomerization of these compounds was investigated in organic solvent. For example, the absorption spectrum of (*S*,*R*,*S*)-**1a** in the initial state exhibited two distinct bands, one below 250 nm and the other one between 300 and 420 nm (Figure 3, top), which are characteristic of molecules having both naphthalene and azoarene chromophores in their structure.[15] The absorption band below 250 nm can be attributed to long-axis polarization (^{1}B transition) of the naphthalene chromophore. The band between 300 and 420 nm corresponds to the $\pi \rightarrow \pi^*$ transitions of the azo chromophore and the short-axis polarizations (^1L_a and ^1L_b) of the naphthalene moieties. Accordingly, the CD spectrum of (*S*,*R*,*S*)-**1a** shows two distinct regions (Figure 3, bottom).[16] The strongest bisignated exciton couplet between 200 and 250 nm is related to the coupling of the two long-axis-polarized (^1B_b) transitions located on distinct naphthalene rings. Some Cotton effects corresponding to azoarene excitations combined with short-axis-polarized (^1L_a and ^1L_b) transitions of binaphthyl groups were observed between 300–420 nm. Subsequently, the solution was irradiated with UV light (365 nm, 30 mW cm^{-2}) and the photoisomerization process was monitored by both absorption and CD spectroscopy. The absorption band between 300 and 420 nm ($\pi \rightarrow \pi^*$ transition) gradually decreased with a concomitant increase in the band around 460 nm ($n \rightarrow \pi^*$ transition), which was evidence of the *trans*–*cis* isomerization of the azoarene units. The photostationary state (PSS$_{365\text{nm}}$) was reached in about 60 seconds, which was indicated by no change upon further irradiation. Dramatic changes were also found in the chiroptical properties as indicated by the CD spectra. A slight intensity decrease was observed in the positive exciton couplet at 225 nm, which must be due to the conformation changes of the azoarene unit. More importantly, the intensity of the $\pi \rightarrow \pi^*$ transition decreased dramatically and a new exciton couplet between 420 and 550 nm was observed, which originated from the $n \rightarrow \pi^*$ transition band of the *cis* isomer. The reverse absorption and CD spectral changes can be achieved by either visible light irradiation at 550 nm or thermal relaxation in the dark (Figure S1). The changes in CD spectra showed that the chiroptical properties of this compound could be modulated by light and that it has potential to be used as a photoresponsive dopant in LCs.

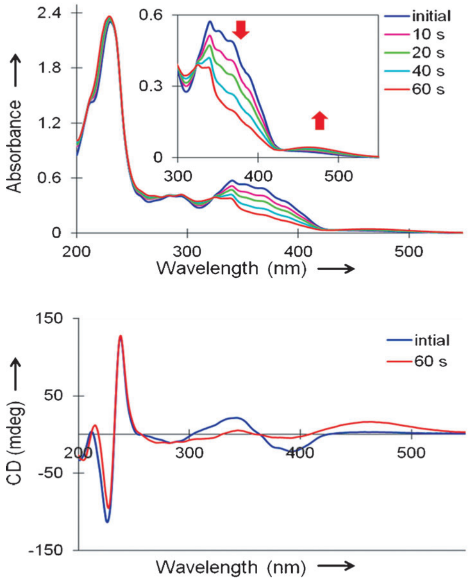

Figure 3. UV (top) and CD (bottom) spectra of chiral dopant (*S*,*R*,*S*)-**1a** (10 µM) in hexane upon UV irradiation at 365 nm.

A chiral compound can impart its chirality to an achiral nematic LC host to form a cholesteric phase. The ability of a chiral dopant to induce the cholesteric phase is defined as HTP and expressed in the equation $\beta_M = 1/(pc)$, where p is the pitch length of the helical superstructure and c is the molar concentration of the chiral dopant. As expected, doping these molecules into an achiral LC host was able to immediately induce the formation of a cholesteric phase, as shown by a characteristic fingerprint texture (Figure S8a).[17] The HTPs of these compounds and the change in HTP were measured using Cano's method in wedge cells.[18] Interestingly, when the wedge cell, filled with 0.27 mol% (*S*,*R*,*S*)-**1a** in 4-cyano-4′-pentylbiphenyl (5CB), was irradiated with UV light at 365 nm, the Cano lines moved outward and disappeared in ten seconds and an apparent nematic phase (infinite-pitch CLC) was observed in the wedge cell as a result of the destruction of the initially induced cholesteric phase (Figure 4a and b). Upon further irradiation, an oily streak texture gradually appeared and the Cano lines were formed again at the PSS$_{365\text{nm}}$ within two minutes (Figure 4c). This cholesteric (N*)–nematic (N)–cholesteric (N*) phase transition sequence is an indication of the inversion of the cholesteric handedness.[9,10] Handedness inversion occurs when the helix of one handedness unwinds, disappears at a certain point, and then forms a helix of the opposite handedness. We also observed the same phase transition sequence in a homeotropic cell. The typical fingerprint texture of the cholesteric phase was clearly observed under polarized optical microscopy at the initial

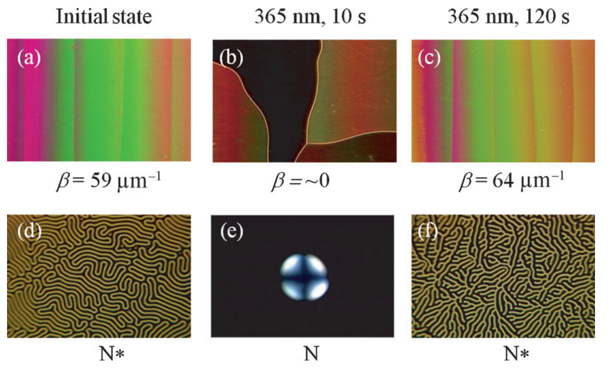

Figure 4. Handedness inversion of 0.27 mol% (*S*,*R*,*S*)-**1a** in 5CB observed in a wedge cell (a–c) and homeotropic cell (d–f) from right-handed CLC (a,d) to left-handed CLC (c,f) through a transient nematic phase (b,e), observed using crossed polarizing microscopy.

state (Figure 4d). Upon UV irradiation at 365 nm, the fingerprint texture disappeared quickly and a transient nematic phase was confirmed with conoscopic observation (Figure 4e). Continued UV irradiation resulted in the reappearance of the fingerprint texture, indicating the formation of another cholesteric phase with opposite handedness (Figure 4f). Notably, the phase transition sequence observed in the wedge cell and the homeotropic cell was reversible upon visible light irradiation at 550 nm as a result of the reverse *cis* to *trans* isomerization of (*S*,*R*,*S*)-**1a**.

The handedness of a cholesteric phase can be examined through the contact method based on the miscibility between two CLC mixtures and the observation of their mixing boundary.[19] When the handedness of these two CLCs are the same, the mixing area will be continuous. Otherwise a nematic gap between them will appear as a discontinuous pattern if they exhibit opposite handedness. Therefore the handedness of one of them is known, the handedness of the other can be determined accordingly. To gain further insight into the handedness inversion during photoisomerization, the handedness of the CLCs induced by (*S*,*R*,*S*)-**1a** were tested with this method. (*S*)-2,2′-Methylenedioxy-1,1′-binaphthyl (MDB) was used as the standard material, which is known to induce a right-handed CLC in nematic LC 5CB owing to the *cisoid* conformation of the bridged binaphthyl.[13a] As shown in Figure S5, the mixture of CLCs induced by (*S*,*R*,*S*)-**1a** and MDB exhibited a continuous pattern, indicating that (*S*,*R*,*S*)-**1a** also induced a right-handed CLC at its initial state. The handedness of (*S*,*R*,*S*)-**1a** in the UV-irradiated state was determined to be left-handed owing to the discontinuous boundary. These results provided direct evidence that the handedness of the CLC induced by (*S*,*R*,*S*)-**1a** inverted upon UV irradiation.

Similar handedness inversion was also observed for compounds (*S*,*R*,*S*)-**1b** and (*S*,*R*,*S*)-**1c** (Figure S7). For comparison, an LC mixture composed of 0.27 mol% of (*R*,*R*,*R*)-**1d** in 5CB was also filled into a wedge cell. A dramatic pitch increase was observed upon light irradiation as evidenced by the distance change between the two Cano lines (Figure S8b,c). The HTP of (*R*,*R*,*R*)-**1d** at the initial state was calculated to be 242 µm^{-1} and decreased to 86 µm^{-1}at the PSS_{365nm}, which was attributed to the conformation change from the *trans* to *cis* isomer and the destabilization of the LC order with the bent shape of the *cis* isomer. Notably, no handedness inversion was observed during this process. Combined with the high HTP in the initial state, this might be due to the collective effect of the three chiral moieties in this compound because they all induced the same handedness.

The HTPs of (*S*,*R*,*S*)-**1a–c** and (*R*,*R*,*R*)-**1d**, in three different nematic LC hosts at different states were evaluated, and the results are summarized in Table 1. The positive sign represents right handedness and the negative sign left handedness. Compounds (*S*,*R*,*S*)-**1a–c**, bearing opposite chiral configurations, were all found to induce the handedness inversion in three LC hosts with moderate to high HTPs at both states, except for (*S*,*R*,*S*)-**1c** in ZLI-1132. The right handedness of (*S*,*R*,*S*)-**1a–c** in the initial state was attributed to the central axially chiral azoarene part, whose derivatives normally exhibit very high HTPs with right handedness.[4b–d] Although the two binaphthyl units induced CLC with left handedness, the combined effect of these three chiral moieties gave an overall right handedness, that is, the azoarene part played a dominant role in the handedness (Figure 5). Upon UV irradiation, the right-handed contribution from the central azoarene part decreased owing to the *trans–cis* isomerization,[4b–d] while the two binaphthyl units still maintained a comparable left-handed contribution with the initial state because they were far away from the azoarene part. Although minor conformational changes of the two binaphthyl units during photoisomerization are possible, when the right-handed contribution decreased significantly, the left handedness became dominant and thus resulted in overall left-handed cholesteric phases (Figure 5). Combined with the high HTPs and the handedness retention of (*R*,*R*,*R*)-**1d**, which has three chiral centers with the same chirality, we concluded that the handedness inversion of (*S*,*R*,*S*)-**1a–c** originated from the conflicting chiralities and the shifting equilibrium between (*R*)-azoarene and (*S*)-binaphthyls.

Table 1: Helical twisting powers (HTPs) of dopants in different LC hosts and the observed changes upon light irradiation.[a]

Dopant	LC host[b]	β_M [molar%$^{-1}$ µm^{-1}] initial	PSS_{UV}	PSS_{vis}	$\Delta\beta_M/\beta_M$[c] [%]
(*S*,*R*,*S*)-**1a**	5CB	+59	−65	+54	210
(*S*,*R*,*S*)-**1a**	E7	+111	−33	+55	130
(*S*,*R*,*S*)-**1a**	ZLI-1132	+32	−14	+22	145
(*S*,*R*,*S*)-**1b**	5CB	+27	−50	+25	283
(*S*,*R*,*S*)-**1b**	E7	+39	−33	+36	185
(*S*,*R*,*S*)-**1b**	ZLI-1132	+34	−17	+30	149
(*S*,*R*,*S*)-**1c**	5CB	+39	−45	+36	216
(*S*,*R*,*S*)-**1c**	E7	+57	−26	+44	145
(*S*,*R*,*S*)-**1c**	ZLI-1132	+89	+22	+78	75
(*R*,*R*,*R*)-**1d**	5CB	+242	+87	+188	64
(*R*,*R*,*R*)-**1d**	E7	+168	+67	+149	60
(*R*,*R*,*R*)-**1d**	ZLI-1132	+102	+26	+92	74

[a] Positive and negative signs represent right- and left-handed helical twists, respectively. [b] The achiral nematic liquid crystals E7, 5CB, and ZLI-1132 are commercially available (see Supporting Information). [c] Percent change in β_M observed in going from the initial state to PSS_{UV}.

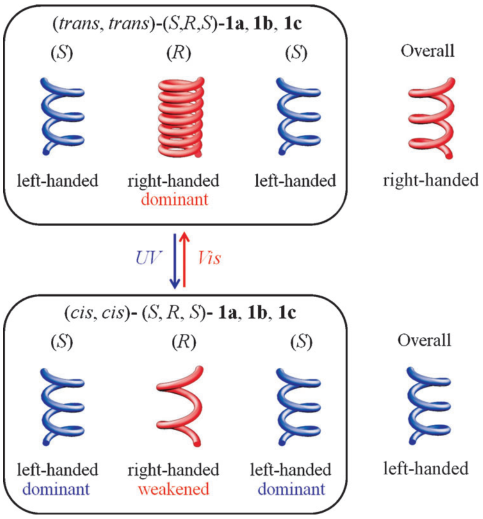

Figure 5. Schematic illustration of the mechanism of handedness inversion in self-organized helical superstructures induced by dopants (*S*,*R*,*S*)-**1a**, (*S*,*R*,*S*)-**1b**, and (*S*,*R*,*S*)-**1c**.

Using different LC hosts for the same dopant resulted in different intermolecular associations between the dopant and the host as revealed by the different HTP values and the change in the magnitude of HTP. It is also clear from Table 1 that these three dopants exhibit a larger change of HTPs in 5CB, while E7 and ZLI-1132 gave higher HTPs at the initial state with right handedness. The spacer lengths between the azoarene and binaphthyl groups in (*S*,*R*,*S*)-**1a–c** have strong effects on the initial HTPs, which might be due to the different steric hindrance and the variance in the binaphthyl conformation. Notably, all the helix inversions in these LC hosts are reversible by visible-light irradiation. The fatigue resistances were also examined by repeatedly switching the LC mixtures between $\mathrm{PSS_{UV}}$ and $\mathrm{PSS_{vis}}$, no obvious degradation was observed after several cycles.

In conclusion, a series of azoarene compounds containing axially chiral moieties with different chiral configurations were synthesized. The chiral conflict and equilibrium shifting between opposite chiral configurations in these compounds was used to promote the handedness inversion of the resulting helical structures. Their handedness inversion was found in different LC hosts and the HTPs for both states were moderate to high. This strategy can be realized by simply changing the terminal chains and spacer lengths of these molecules, which allows us to understand the structure–property relationships. The strategy demonstrated herein could provide insights for developing photoresponsive liquid-crystal materials for applications and further stimulate the rational design of materials for handedness inversion.

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