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Long-Lived Supramolecular Helices Promoted by Fluorinated Photoswitches

He Huang, Tetiana Orlova, Benjamin Matt, and Nathalie Katsonis*

Chiral azobenzenes can be used as photoswitchable dopants to control supramolecular helices in liquid crystals. However, the lack of thermal stability of the *cis*-isomer precludes envisioning the generation of long-lived supramolecular helices with light. Here, this study demonstrates thermally stable and axially chiral azobenzene switches that can be used as chiral dopants to create supramolecular helices from (achiral) nematic liquid crystals. Their *trans*-to-*cis* photoisomerization leads to a variation of helical twisting power that reaches up to 60%, and the helical superstructure that is engineered with light displays a relaxation time that reaches tens of hours. These results demonstrate that combining *ortho*-fluorination with axial chirality in molecular photoswitches constitutes an efficient strategy to promote long-lived helical states. Further, this approach shows potential to design supramolecular machines that are controlled by light entirely.

1. Introduction

Molecular photo-switches are dynamic and versatile building blocks for the design of wholly synthetic supramolecular^[1] and macromolecular machines.^[2,3] However, making full use of their potential for the design and synthesis of wholly synthetic soft machines will require the development of strategies by which their photoisomerization is amplified from the molecular level across length scales, and ultimately up to the macroscopic level, by taking advantage of cooperative effects.^[4,5] Liquid crystals provide versatile, sensitive, and anisotropic supramolecular matrices that respond with collective effects to small changes in their composition and thus they can amplify molecular chirality and motion efficiently into optical or mechanical responses.^[6] Coupling molecular photoswitches with liquid crystals has allowed developing light-responsive molecular systems with applications ranging from optical memory writing^[7] to colorful displays.^[8] Combined with (helix-based) cholesteric liquid crystals, molecular photoswitches have allowed creating and manipulating chiral topological structures,^[9,10] changing reflexion colors and polarization,^[11–13] detecting catalytic reactions,^[14] and developing soft rotating devices.^[5] When embedded in liquid crystal networks covalently, molecular photoswitches have mediated complex shape transformations,^[15,16] and the conversion of

light into work and power by soft polymer machines has been demonstrated also.^[17]

Light-responsive cholesteric liquid crystals can be prepared by dissolving a small percentage of chiral photoswitches in a (achiral) nematic liquid crystal host^[4,18] (Figure 1). The propensity of these photoswitches, used as dopants, to induce a twist in a given host is characterized by their helical twisting power (HTP), defined as $\beta = (p \times c \times ee)^{-1}$, where p is the pitch and corresponds to a full 360° rotation of the molecules along the helical axis, c is the concentration of the dopant in wt%, and ee is the enantiomeric excess of the dopant. Chiral switches are typically characterized by large twisting powers for their chirality and can be amplified across length scales effectively.^[6]

Azobenzenes are typically used as switchable dopants because their *trans*-*cis* photoisomerization is associated with large changes in both the geometry and the dipole moment of the molecule. While rod-like *trans*-azobenzenes are compatible with the nematic order, the bent-like *cis*-molecules disturb this molecular order significantly. Consequently, the HTP of the *trans* and the *cis* isomers are remarkably different. Moreover, coupling azobenzenes to elements of axial chirality yields both a large HTP in the ground state and a large variation of HTP under irradiation with light, compared to chiral azobenzenes that display point chirality only.^[11,19–22] Light-driven helix inversion has also been reported, when chiral azobenzene dopants with axial chirality were used as dopants.^[23–25] However, the lack of thermal stability of the *cis*-isomer remains a limitation to reaching the full potential of complex dynamic behavior in these supramolecular systems.

Fluorinated azobenzenes display larger thermal stability than their classical counterparts, primarily because the repulsion between the nitrogen lone pairs that destabilizes the *cis*-isomer is lifted by electron-withdrawing effect of the fluorine atoms in *ortho*-position.^[26–29] Here, we combine the axial chirality of a binaphthyl moiety with *ortho*-fluorination of an azobenzene moiety in molecular photoswitches that induce supramolecular helices in liquid crystals in both forms, and thus we demonstrate the photo-engineering of long-lived supramolecular helices in soft matter.

2. Results and Discussion

Molecules **1a** and **1b** were synthesized from commercially available starting materials. Their photochemistry and performance as dopants were investigated by comparing them to the reference azobenzenes **2a**^[19] and **2b**^[20,30] in the same

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Figure 1. A photoswitch with axial chirality allows forming a cholesteric liquid crystal and controlling its helix-based structure with light.

conditions (Figure 2; Figure S1, Supporting Information). The chemical structures of the intermediate and final compounds were identified by ^1H NMR, ^{13}C NMR, and high-resolution mass spectrometry (Figures S2–S5, Supporting Information).

Solutions of **1** and **2** in chloroform were irradiated with UV light ($\lambda = 365$ nm), which led to *trans*→*cis* isomerization, as evidenced by a decrease in the π → π^* absorption band corresponds to the (*trans, trans*)-azobenzene chromophore ($\lambda_{\text{max } 1a} = 348$ nm, $\lambda_{\text{max } 1b} = 348$ nm, $\lambda_{\text{max } 2a} = 358$ nm, and $\lambda_{\text{max } 2b} = 356$ nm) and an increase in the n → π^* absorption band around 450 nm^[26,27] (Figure S6, Supporting Information). Since the photoswitches incorporate two azo moieties that are decoupled from each other electronically, irradiation with light induces the formation of photoisomers containing either one or two *cis*-moieties. The photoswitching sequence is thus (*trans, trans*) → (*trans, cis*) → (*cis, cis*) (Figure 3). Once the photostationary state is reached, 27% of the azobenzene moieties have switched into the *cis*-form for **1a**, and 40% for **1b**. These photostationary ratios compare well with the ratios we measured for **2a** and **2b** (Figure S7, Supporting Information), while remaining moderate.

The absorption spectra suggest that *ortho*-fluorination affects the n → π^* transition equally in the *trans* and in the *cis* form, and therefore, the n → π^* bands overlap similarly in the fluorinated and the nonfluorinated switch (Figure S6,

Figure 3. Photoswitching sequence for the chiral molecules used as dopants.

Supporting Information). Due to this specificity of the n → π^* transition, it is not possible to switch dopants **1a** and **1b** in both directions with visible light selectively.^[27] However, while fluorination does not lift the similarity between the n → π^* transition of the *trans*-form and the *cis*-form, its effect is visible in the blue-shift of the π → π^* absorption bands of fluorinated **1a** and **1b**, compared to their classical counterparts **2a** and **2b** (≈ 10 nm). We conclude that an electron-withdrawing effect does take place by partial *ortho*-fluorination, and this effect is likely to stabilize the *cis*-form by minimizing the repulsion between lone pairs.

Figure 2. Molecular structure of the fluorinated photoswitches used as dopants and their classical counterpart.

Table 1. Half-life time of the thermal relaxation $t_{1/2}$ for the photo-switches in solution, and when used as chiral dopants in liquid crystals.

Dopant	$t_{1/2}^{a,b)}$ [h] in CHCl_3	Liquid crystal	$t_{1/2}^{a,b)}$ [h] in liquid crystal	$t_{1/2}^{a,c)}$ [h] in liquid crystal
1a	13.6	E7	35.6	28.0
		MLC 6608	59.3	44.1
1b	2.7	E7	33.6	41.0
		MLC 6608	67.9	93.6
2a	1.2	E7	8.5	3.7
2b	0.4	E7	5.8	7.9

^{a)}All half-life times of relaxation were measured at 22 °C; ^{b)}Monitored by changes in UV-vis absorption spectra; ^{c)}Monitored by changes in the cholesteric pitch, as measured from a wedge cell.

Further, we have investigated the *cis*-to-*trans* relaxation kinetics of the switches in solution. Monitoring of the increasing in $\pi \rightarrow \pi^*$ absorption band under thermal relaxation shows that, in both molecular switches, the *cis*-to-*trans* relaxation follows first-order kinetics. As expected from the presence of fluorine atoms, the thermal relaxation of *cis*-1 is slower than that of *cis*-2 (Table 1; Figure S8, Supporting Information). However, both *cis*-1a and *cis*-1b display only a moderate thermal stability compared to the thermal stability reported for tetra-fluorinated azobenzenes.^[26,27] This moderate thermal stability likely originates in the electron-donating resonance effect from the naphthyl group, as a counterpoint to the electron-withdrawing inductive effect from the fluorine atoms.

Next, the photoswitches were investigated in nematic liquid crystals, starting with the commercially available mixture E7 (Figure S9, Supporting Information). In this liquid crystalline environment, UV irradiation of all four compounds results in a decrease of the $\pi \rightarrow \pi^*$ absorption band. The investigation of the *cis*→*trans* relaxation (Figure S10, Supporting Information) reveals that, independently on the presence of fluorine, the half-life time of the *cis*-form is

longer in the liquid crystalline phase than in solution. This stabilization in the liquid crystal likely originates in the combined effect of viscosity, high π -electron density and decreased molecular degree of freedom in the anisotropic environment of the liquid crystal. The suitability of **1a** and **1b** as chiral dopants was also investigated in MLC 6608, a liquid crystal that is nematic at room temperature with a negative dielectric anisotropy, while E7 displays a positive dielectric anisotropy. Both molecular photoswitches show longer half-life times in MLC 6608 than in E7 (Table 1; Figures S11 and S12, Supporting Information).

The HTP of the dopants was determined by using the Grandjean-Cano wedge cell method.^[31] In all samples, the cholesteric helix was left-handed. In E7, the initial HTP values for fluorinated dopants **1a** and **1b** are lower than for the corresponding reference molecules **2a** and **2b**, probably because the fluorine atoms modify the dipole moment of the switches. The photoinduced variation of HTP is modest in the presence of the *ortho*-fluorinated switches. However, the thermal relaxation of the light-induced cholesteric helix, from the photostationary helix back to the initial helical organization, reveals to be one order of magnitude slower for **1** than for **2** (Figure 4, Table 1; Figures S13 and S14, Supporting Information). In MLC 6608, **1a** and **1b** showed similar HTP values and similar amplitudes of variation after photoisomerization, while the **1b** showed two times longer half-life time of pitch relaxation (Table 2; Figures S15 and S16, Supporting Information).

Noticeably, for switches **1a** and **2a**, the half-life time is smaller when measured by pitch change, compared to when it is measured by changes in absorbance. For compounds with extended rigid arms **1b** and **2b**, the opposite was observed (Table 1). In principle, the readjustment of the cholesteric helix, in response to molecular isomerization, depends on the elastic properties of the liquid crystal and on the thickness of the sample.^[32] Here, we thus anticipate that the difference in response of the helices relates to the elastic properties of the liquid crystal, combined with the effects of liquid crystalline confinement.

Figure 4. UV irradiation and thermal relaxation of the liquid crystal helices induced by dissolving 1 wt% of photoswitch **1b** in the nematic liquid crystal E7. (Scale bar = 100 μm , wedge cell $\tan \theta = 0.0115$.)

Table 2. Helical twisting power (HTP) for azobenzene dopants in the *trans* form and at the photostationary state.

Dopant	Liquid crystal	HTP initial [$\mu\text{m}^{-1}\text{ wt}\%^{-1}$]	HTP at PSS [$\mu\text{m}^{-1}\text{ wt}\%^{-1}$]	ΔHTP [%]
1a	E7	−20.1	−8.1	60
	MLC 6608	−31.8	−17.7	44
1b	E7	−46.3	−19.0	56
	MLC 6608	−37.0	−18.0	51
2a	E7	−40.6	−2.7	93
2b	E7	−94.3	−23.4	75

3. Conclusion

We have designed and synthesized *ortho*-fluorinated and axially chiral molecular photoswitches that can be used as dopants in liquid crystals, where they induce the formation of self-organized helical superstructures efficiently. The *trans*-to-*cis* photoisomerization of these molecules is accompanied by a variation of HTP that reaches up to 60%, and the supramolecular helix they generate under irradiation with light is stable thermally, with a relaxation time of tens of hours. Besides their efficiency as chiral dopants and thermal stability in both *trans* and *cis* forms, we also note that in these fluorinated switches, the $n \rightarrow \pi^*$ transition are similar for both photoisomers; therefore, it is not possible to address them with visible light selectively. The switches also show moderate photoconversions. Overall, combining *ortho*-fluorination with axial chirality allows designing photoswitches that promote light-driven and long-lived helical states in liquid crystals. We envision that these versatile and light-responsive helices can be incorporated into complex molecular systems, to mediate the development of soft machines that are controlled by light entirely.^[33]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

chirality, light, liquid crystals, molecular switches

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