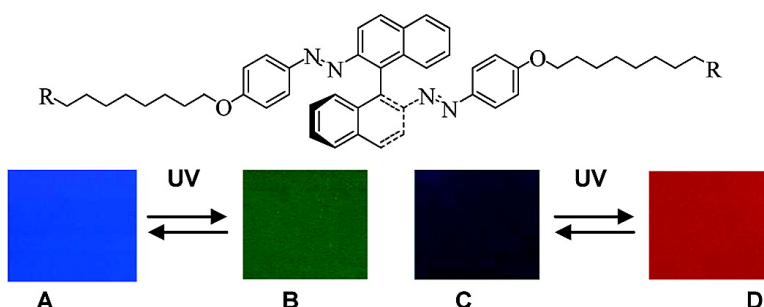


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Reversible Photoswitchable Axially Chiral Dopants with High Helical Twisting Power

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The development of reversible optical memory and light-driven chiral molecular switches is attracting tremendous interest since they hold a great promise in applications as well as fundamental science.¹ A promising solution lies in the photoresponsive chiral nematic (cholesteric) phase whose unique helical structures and physical properties can be tuned upon light irradiation. Such a phase can be achieved by doping both azo molecules and chiral molecules into a nematic liquid crystal host.² *trans*-Azobenzene is thermodynamically more stable than *cis*-azobenzene by ca. 56 kJ/mol; however, irradiation with ultraviolet light at a wavelength of about 360 nm leads to its *trans*–*cis* isomerization. The reverse process from *cis* to *trans* isomer can occur thermally or photochemically with visible light. Since the physical and chemical properties of the azobenzene configurational isomers are different, the reversible optically induced switching effect has been the basis for many functional molecules and materials with applications in photonics and liquid crystal displays.^{3–6} It is also well-known, that when a chiral molecule is dissolved in an achiral nematic liquid crystal, its molecular chirality is transferred to the nematic solvent which then organizes into a macroscopic helical architecture that reflects light according to Bragg's law. The wavelength λ of the selective reflection is defined by $\lambda = np$, where p is the pitch length of the helical structure and n is the average index of refraction of the liquid crystal material. The ability of a chiral dopant to twist the nematic liquid crystal phase is defined as helical twisting power (HTP) _{β} according to the equation: $\beta = (pc)^{-1}$, where c is either weight concentration or molar fraction of the chiral dopant. The isomerization upon photo irradiation can control the HTP and the helical pitch of the cholesteric phases, providing the tool for optical display addressing.

Current chiral dopants are often used at concentrations of 20% or higher in a nematic host since chiral dopants available today have twisting powers typical of $\beta < 15 \mu\text{m}^{-1}$.⁷ The addition of a high concentration of chiral molecules and azo molecules often causes instability of the resulting liquid crystalline phase and can alter beneficial physical properties.⁸ A logical route to overcome the disadvantages is to develop a chiral azo molecule that has high helical twisting power and maintains good solubility in a liquid crystal host. However, only a few developments of chiral azo molecules have been reported to date, compared with numerous azo dyes and chiral dopants.⁹

Here we report the synthesis of four reversible photoswitchable axially chiral dopants **3** with unusually high helical twisting power. To our best knowledge, these are the first four compounds with the general structure **3** (Figure 1) to be synthesized. The interest behind the design of these new photoresponsive chiral dopants containing the well-known axially chiral 1,1'-binaphthyl group mainly results from the unique axially chiral structure originating from the rotational barrier around the naphthyl–naphthyl bond¹⁰ and the distinct optical properties of the azo moiety. Meanwhile,

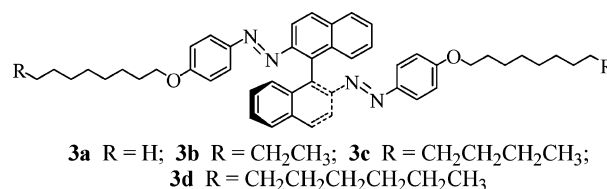


Figure 1. Molecular structures of the axially chiral azo dopants **3**.

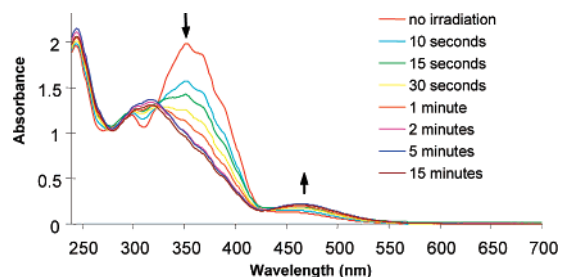


Figure 2. UV–vis absorption spectra of **3b** (32 $\mu\text{g/mL}$) in hexane under UV irradiation (365 nm at 0, 10 s, 15 s, 30 s, 1 min, 2 min, 5 min, and 15 min).

the introduction of two flexible long alkoxy chains can reduce its melting point, greatly increase its solubility in a nematic host, and stabilize the molecular orientations of the resulting chiral nematic phase.¹¹

These chiral dopants **3a–d** are chemically and thermally stable, and exhibit the expected reversible photoswitchable behavior in both organic solvent and liquid crystal media. Dark incubation of a solution of **3b** in hexane served to maximize the absorption at 352 nm corresponding to the (*trans,trans*)-azobenzene chromophore. Irradiation of this solution with 365-nm light resulted in clean photoisomerization to (*cis,cis*)-**3b**, as evidenced by a decrease in the absorbance at 352 nm and an increase in absorbance at 458 nm (Figure 2). Due to the molecules having two azo linkages, ultraviolet irradiation leads to reversible *trans*–*cis* isomerization of azo configurations, producing two other isomers containing one or two *cis* configurations, respectively. The sequence of photochemical switches of the three isomers is (*trans,trans*)-**3** \rightarrow (*trans,cis*)-**3** \rightarrow (*cis,cis*)-**3**. The reverse process from (*cis,cis*)-**3** \rightarrow (*trans,cis*)-**3** \rightarrow (*trans,trans*)-**3** can occur thermally or photochemically with visible light. For example, a photostationary state from (*trans,trans*)-**3b** to its (*cis,cis*)-isomer was reached within approximately 2 min under irradiation at 365 nm (Figure 2). Reversion of (*cis,cis*)-**3b** to its (*trans,trans*)-isomer was reached within approximately 24 h at room temperature in the dark after irradiation of its solution with 365-nm light resulted in complete photoisomerization to (*cis,cis*)-**3b**.

The reversible photoinduced conversion of (*trans,trans*)-**3** to (*cis,cis*)-**3** was also clearly observed by NMR spectroscopy and thin-layer chromatography (TLC). The OCH₂ group in *trans*-**3** and *cis*-**3** in CDCl₃ appears as triplet at δ about 3.88 and 4.10, respectively. The changes of chemical shifts in the phenyl and naphthyl regions of the spectrum were also observed.

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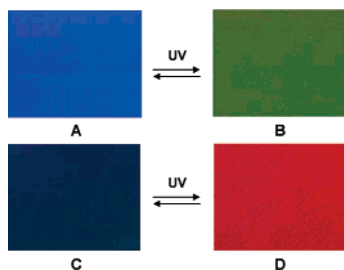


Figure 3. Crossed polarized optical texture micrograph of the mixture of 2.5% (A) and 5.0% (C) **3b** in 5CB at 24 °C (A and C: before UV irradiation; B and D: after UV irradiation for 10 min).

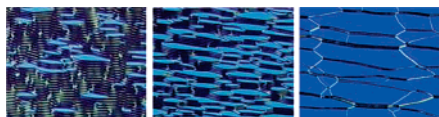


Figure 4. Some change (left to right) of crossed polarized optical texture micrograph of the 2.5% **3b** in 5CB after removal of UV light.

Table 1. HTP of the Chiral Dopants in E7 Nematic Host in the Initial (*trans-trans*) Configuration

dopant	β (molar) μm^{-1}	β (wt %) μm^{-1}
3a	153	60
3b	158	57
3c	172	57.5
3d	166	53

As expected, doping the chiral dopant **3** in an achiral nematic liquid crystal host can induce a chiral nematic mesophase. For example, we used the compound **3b** as a chiral dopant to conventional achiral nematic liquid crystal 4'-pentyl-4-biphenylcarbonitrile (5CB) at the composition of 2.5% and 5.0% **3b** in the 5CB host. The two mixtures were capillary-filled into 5 μm thick parallel cells. A homogeneous aligned chiral nematic mesophase in both cells was observed at 24 °C under a crossed polarized microscope (Figure 3). Upon UV irradiation at 365 nm, the color of the thin film texture in the 2.5% cell changed from light-blue to green, and the color of the thin film texture in the 5.0% cell changed from dark-blue to red. Removal of UV light immediately leads to the reverse process, passing through different chiral nematic phases with a characteristic oily, streaked texture (e.g., Figure 4). The reversion to the texture in Figure 3 was reached within approximately 24 h at room temperature in the dark. By photochemically controlling the ratio of *trans/cis* isomers, their reflective wavelength can be continuously varied, making it possible to tune the color of the thin film over the entire visible region.

Their helical twisting powers were measured in the usual manner by dissolving a known quantity of material in a nematic liquid crystal and measuring the induced helical pitch length, in this case, by observing the wavelength of visible light reflected from the Bragg reflective material. The nematic E7, which is a eutectic mixture of liquid crystal components commercially designed for display applications, was used as the host. All **3a-d** compounds induce left-handed cholesteric phases. Of significance is the unusually high HTP values the chiral materials **3** exhibit (Table 1).

A display cell for photo imaging was constructed using two glass substrates (2 in. \times 2 in.). The inner surfaces of the two pieces were coated with a polyimide to serve as an alignment layer. The substrates are held together with a gasket material and spacers to maintain a cell thickness of 5 μm . A small opening is made in the gasket material for filling the cell with liquid crystal. A liquid crystal mixture was prepared with a 6.0% chiral compound **3b** and 94% nematic host. The surface of the back side of the cell is painted with black paint to create a contrast with a bright iridescent Bragg



Figure 5. Illustration of an optically addressed image with negative photo mask. (Left) Regular photograph of the original digital image. (Middle) Negative photo mask made of PET. (Right) Image optically written on the display cell.

reflective color from the chiral nematic material when viewed from the other side of the cell.

An image was addressed on the display cell using UV light with a negative photo mask made of 10 mil PET placed on the top of the display and exposed to UV light ($637 \mu\text{W}/\text{cm}^2$ at $\lambda_{\text{max}} = 365 \text{ nm}$) for 20 min. Depending on the optical density of the mask, certain areas were exposed with different intensities of light, resulting in an image composed of a variety of colors due the various shifts in pitch length. Figure 5 shows a photo of an original image, the negative mask, and the resulting image on the display cell.

In conclusion, four photoswitchable azo axially chiral compounds with high helical twisting power were synthesized. Their reversible photoresponsive properties were well demonstrated. These materials are found suitable for dopants in chiral nematic materials for applications in novel optically addressed displays, i.e., photodisplay. Optically addressed images were demonstrated. The dopants were sufficiently responsive to an addressing light source so that a high-resolution image with gray scale could be imaged in a few seconds of irradiation time. It was further found that an image could be retained on the screen at room temperature for 24 h before being thermally erased. The high solubility of these materials in a nematic host is also of commercial interest for stability in display applications. It is worth noting here that the photo display device can display a high-resolution image without the need of an attached drive and control electronics, substantially reducing the cost of the display unit for use in applications where paper is currently used.

Acknowledgment. The work is supported by NSF OII-0610809 and Ohio Board of Regents under its Research Challenge program.

Supporting Information Available: Synthesis, *trans-cis* isomerization, optical images, and light sensitivity, response times and relaxation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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