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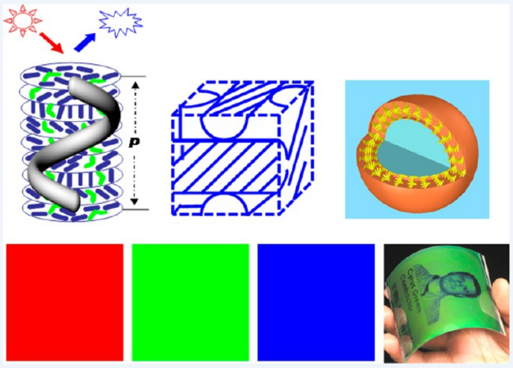
Light-Directing Chiral Liquid Crystal Nanostructures: From 1D to 3D

Hari Krishna Bisoyi and Quan Li*

Liquid Crystal Institute and Chemical Physics Interdisciplinary Program, Kent State University, Kent, Ohio 44242, United States



CONSPECTUS: Endowing external, remote, and dynamic control to self-organized superstructures with desired functionalities is a principal driving force in the bottom-up nanofabrication of molecular devices. Light-driven chiral molecular switches or motors in liquid crystal (LC) media capable of self-organizing into optically tunable one-dimensional (1D) and three-dimensional (3D) superstructures represent such an elegant system. As a consequence, photoresponsive cholesteric LCs (CLCs), i.e., self-organized 1D helical superstructures, and LC blue phases (BPs), i.e., self-organized 3D periodic cubic lattices, are emerging as a new generation of multifunctional supramolecular 1D and 3D photonic materials in their own right because of their fundamental academic interest and technological significance. These smart stimuli-responsive materials can be facilely fabricated from achiral LC hosts by the addition of a small amount of a light-driven chiral molecular switch or motor. The photoresponsiveness of these materials is a result of both molecular interaction and geometry changes in the chiral molecular switch upon light irradiation. The doped photoresponsive CLCs undergo light-driven pitch modulation and/or helix inversion, which has many applications in color filters, polarizers, all-optical displays, optical lasers, sensors, energy-saving smart devices, and so on.

Recently, we have conceptualized and rationally synthesized different light-driven chiral molecular switches that have very high helical twisting powers (HTPs) and exhibit large changes in HTP in different states, thereby enabling wide phototunability of the systems by the addition of very small amounts of the molecular switches into commercially available achiral LCs. The light-driven chiral molecular switches are based on well-recognized azobenzene, dithienylcyclopentene, and spirooxazine derivatives. We have demonstrated high-resolution and lightweight photoaddressable displays without patterned electronics on flexible substrates. The wide tunability of the HTP furnishes reflection colors encompassing the whole visible spectrum and beyond in a reversible manner. Photomodulation of the helical pitch of the CLCs has been achieved by UV, visible, and near-infrared (NIR) light irradiation. NIR-light-induced red, green, and blue (RGB) reflections have been leveraged only by varying the power density of the IR laser. Some chiral switches are found to confer helix inversion to the cholesteric systems, which qualifies the CLCs for applications where circularly polarized light is involved. Dynamic and static primary RGB reflection colors have been achieved in a single film. LC BPs have been fabricated and investigated in the context of self-organized 3D photonic band gap (PBG) materials, and dynamic phototuning of the PBG over the visible region has been achieved. Omnidirectional lasing and tuning of the laser emission wavelength have also been attained in monodisperse photoresponsive CLC microshells fabricated by a capillary-based microfluidic technique.

This Account covers the research and development in our laboratory starting from the design concepts and synthesis of photodynamic chiral molecular switches to their applications in the fabrication of photoresponsive CLCs and BPs. Potential and demonstrated practical applications of photoresponsive CLCs, microshells, and BPs are discussed, and the Account concludes with a brief forecast of what lies beyond the horizon in this rapidly expanding and fascinating field.

1. INTRODUCTION

Nature's art of manifesting chirality from microscopic to mesoscopic levels remains an unchallenged school of inspiration. Supramolecular helical structures are ubiquitous in nature and form the basis of many biological structures and functions. For example, the α-helix of peptides, the double helix of DNA, and the triple helix of collagens are essential and elegant biological chiral structures.[1] Nature has evolved both dynamic and static helical organizations that possess different functional and useful structural attributes. The double helix of DNA represents a dynamic helical superstructure that carries genetic information, whereas beetle exoskeletons represent examples of static helical organization that exhibit magnificent and brilliant structural colors.[2] These have inspired chemists to develop novel materials not only to reveal the structure—property correlation but also to explore their use in diverse technological applications. In this context, cholesteric liquid crystals (CLCs), otherwise known as chiral nematic phases, are unique functional materials with helical organization of mesogenic molecules that can be made both dynamic and static.[1−8] The cholesteric phase was the first liquid crystal (LC) phase to be recognized as a different and distinct state of matter. CLCs are characterized by both handedness and the

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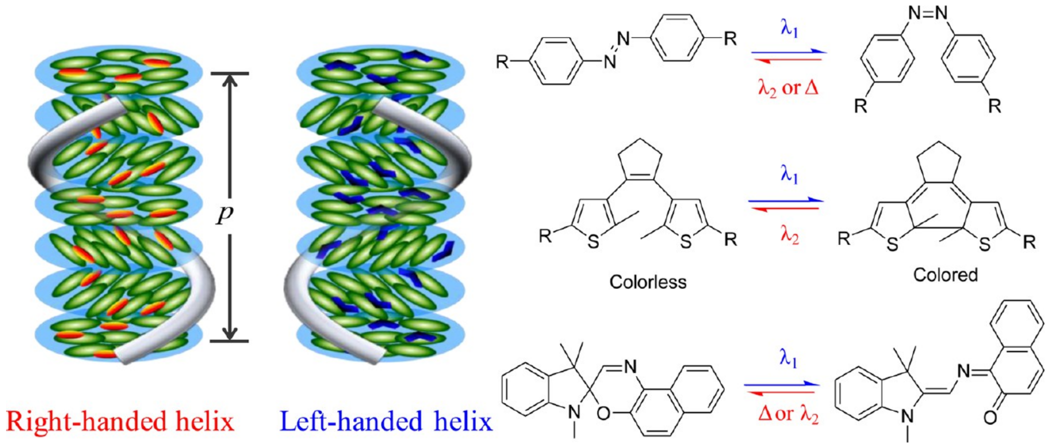


Figure 1. Schematic presentation of the helical superstructure of CLCs (left) and examples of photoisomerizable groups in light-driven chiral molecular switches (right).

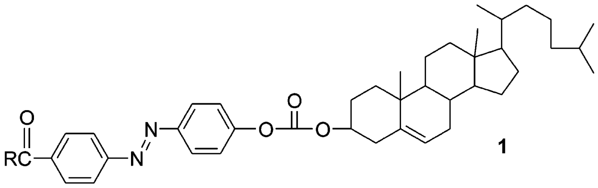
helical pitch, p. Handedness describes the direction in which the molecular orientation (director) rotates along the helical axis, and p is defined as the distance over which the director rotates by a full 360° (Figure 1 left). The most important property of CLCs is the selective reflection of circularly polarized light (CPL) according to Bragg's law. The reflection wavelength can be determined from the relation $\lambda = np$, where n is the average refractive index of the LC medium. When the pitch of the CLC is on the order of the wavelength of visible light, the CLC selectively reflects colored light.[9−12] Consequently, the periodic dielectric helical superstructures of CLCs have been regarded as self-organized one-dimensional (1D) photonic band gap (PGB) materials, and LC blue phases (BPs), i.e. self-organized three-dimensional (3D) periodic cubic lattices, have been considered as dynamic 3D PBG materials.[12−15] Stimuli-induced pitch change and the resulting reflection wavelength tuning of CLCs have found numerous and widespread applications in color filters and reflectors, polarizers, tunable lasers, sensing and imaging, etc. CLCs have also become known for their applications in LC displays (LCDs), in surface thermography and thermometers, and as chiral reaction media, among others.[9−19]

CLCs can be obtained directly from chiral mesogens or by the addition of nonracemic chiral molecules to achiral nematic LCs (NLCs). However, the most recent practice has been to add light-driven chiral switches to NLCs to fabricate dynamic photoresponsive CLCs. It should be noted that NLCs, as elastic anisotropic media, efficiently transfer and amplify the chirality of the dopants, resulting in helical superstructures.[3,4] The photoresponsive CLCs exploit the benefits of light stimuli such as the ease of spatial, temporal, and remote control of the irradiation under ambient conditions. The ability of a chiral molecule to impart a twist to an NLC is quantified in terms of the helical twisting power (HTP), β, which is expressed by the equation $\beta = 1/(pc)$, where c is the molar concentration of the chiral switch. Photoisomerization of the chiral switch results in changes in the molecular conformation and HTP, which may lead to a change in the pitch or handedness of the CLC. A critical challenge in this endeavor is the design and synthesis of photoresponsive chiral molecular switches with high HTP values that display large differences in HTP in their different isomeric states in addition to helix-inversion capabilities.[17,18] High HTP values reduce the necessary concentrations of the dopants, while large differences in HTP of the dopants enable wide-range pitch tunability of the photoresponsive CLCs. In this brief Account, we present the research advancements by our lab in the design and synthesis of photoisomerizable exotic chiral molecular switches possessing exceptionally high HTPs, large variations in HTP, and the ability to cause helix inversion in photoresponsive CLCs and BPs. We focus here on the commonly employed azobenzene-, dithienylcyclopentene-, and spirooxazine-based light-driven chiral molecular switches (Figure 1 right) for the induction and manipulation of photoresponsive CLC (1D photonic crystal) and BP (3D photonic crystal) systems and their consequent display and beyond-display applications. The changes in HTP of the chiral switches and their capability to confer helix inversion in the induced cholesteric phases are highlighted and discussed in light of their molecular interaction and geometry changes wherever appropriate.

2. CHIRAL AZOBENZENES IN LC NANOSTRUCTURES

Azobenzene-based molecular switches possess the unique feature of reversible trans−cis isomerization upon light irradiation, which can cause large conformational and polarization changes intramolecularly. The trans form of azobenzene has a rodlike structure that can stabilize the LC superstructure, whereas its cis form has a bent structure that generally destabilizes the LC superstructure. As a result of the dramatic difference in molecular geometry of the trans and cis forms, the HTPs of these geometric isomers are dramatically different, which in turn enables optical tuning of the cholesteric pitch and hence the PBG. Generally in a CLC mixture containing a chiral azobenzene, the HTP of the chiral switch depends on its molecular structure, the nature of the chirality, and the interaction with host molecules. We designed and synthesized compounds **1** containing the well-known mesogenic cholesteryl group and an azobenzene moiety linked through a short spacer (Scheme 1).[20] As expected, a sequence of mesophases, including a CLC phase, were observed in these compounds. These switches have good solubility in the common commercially available achiral LC 5CB, so they could be used as light-driven chiral switches to induce CLCs; however, their HTP values were found to be very low. Figure 2 shows the polygonal fingerprint texture of the induced cholesteric phase, which undergoes an isothermal phase transition to the isotropic phase upon UV irradiation.

Scheme 1. Azobenzene-Containing Chiral LCs 1



1

R = CH_3 or CH_3CH_2

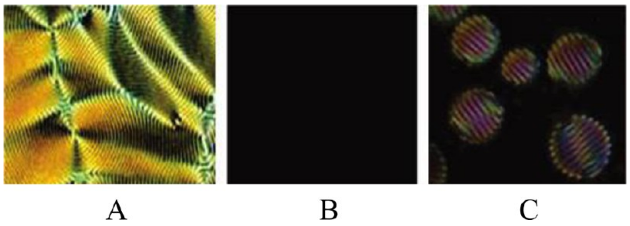
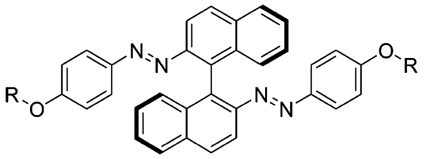


Figure 2. Photostimulated phase transitions in 5CB by doping with **1**. Reproduced from ref 20. Copyright 2005 American Chemical Society.

Scheme 2. Axially Chiral Azobenzene Molecular Switches 2



2a : R = C_8H_{17}; **2b** : R = $C_{10}H_{21}$; **2c** : R = $C_{12}H_{25}$; **2d** : R = $C_{14}H_{29}$

This initial observation of low HTPs was not impressive, so we turned our attention to introducing axial chirality into azobenzene-containing switches. It is interesting that azobenzenes with axial chirality usually show more efficient ability to induce CLC phases than azobenzenes with tetrahedral chirality. Therefore, chiral azobenzene switches **2** incorporating axially chiral binaphthyl units (Scheme 2) were designed and synthesized.[21] It was found that these reversible photoswitches possess very high HTPs in the room-temperature achiral LCs 5CB and E7. Doping of a small quantity of the switches afforded photoresponsive CLCs. A display cell for photoimaging was constructed, and an image was addressed with the help of UV light using a photoresponsive cholesteric mixture in the cell. Figure 3 shows a photograph of an original image, the negative mask, and the resulting photoaddressed image on the display cell. It is worth noting that the photodisplay devices demonstrated here can display high-resolution images without the need of patterned electronics, hence substantially reducing the cost of the display unit. Subsequently, we for the first time developed and demonstrated novel photoaddressed bistable cholesteric displays using the combination of a simple electrode structure and photoaddressable azobinaphthyl chiral switches.[22,23] These displays are inherently high-resolution, require no patterned electronics, and can be made flexible. Such optically addressed cost-effective photodisplays are shown in Figure 4; one display is addressed with the standard multiplexing electronics, while the second display is simply photoaddressed.

Figure 3. Illustration of an optically addressed image with a negative photomask. Reproduced from ref 21. Copyright 2007 American Chemical Society.

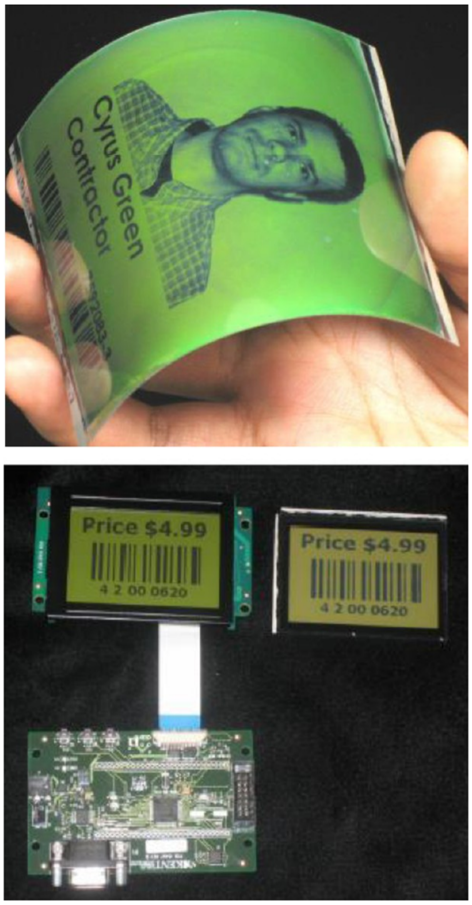


Figure 4. Photodisplays fabricated from photoresponsive CLCs: (top) a flexible photodisplay and (bottom) a conventional electrically addressed display with attached bulky and costly electronics (left) compared with a photodisplay showing the same image without the added electronics (right). Reproduced with permission from ref 22. Copyright 2008 Society for Information Display.

Because of its high HTP, light-driven chiral switch **2d** was shown to enable selective-reflection phototuning of more than 2000 nm in a CLC.[24] The phototuning range and rate as functions of switch concentration, light intensity, and CLC thickness were also investigated. In this work, tuning of the selective reflection over the visible, NIR, and short-wave IR spectral regions was achieved in a single CLC cell (Figure 5).

A cholesteric mixture that can be tuned with light and an applied electric field was fabricated by adding **3b** (Scheme 3) to the NLC ZLI-4788.[25] Interestingly, the reflection of the CLC is red-shifted with UV light and blue-shifted with an applied direct-current (DC) electric field; however, upon removal of the DC field, the notch position can be restored. Similarly, electrically switchable, photoaddressable CLC reflectors were developed from a mixture of the NLC E44 and chiral switch **3b**.[26] It should be noted that electric fields are able to reorient

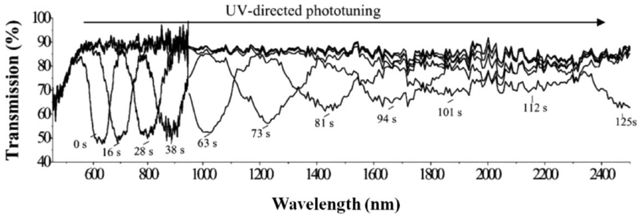
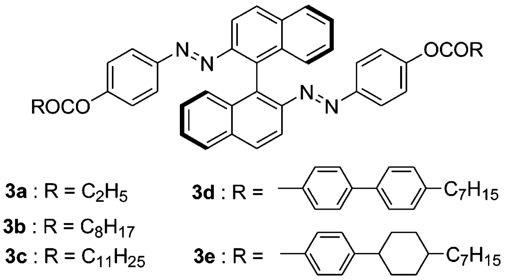


Figure 5. Tuning of the reflection wavelength of a CLC over a range of 2000 nm. Reproduced with permission from ref 24. Copyright 2009 Wiley-VCH Verlag GmbH & Co.

Scheme 3. Axially Chiral Azobenzene Switches 3



3a : R = C_2H_5
3b : R = C_8H_{17}
3c : R = $C_{11}H_{25}$
3d : R = —C_7H_{15}
3e : R = —C_7H_{15}

the helix axes and dilate the pitch of the CLCs because of the dielectric anisotropy of NLCs. By polymer stabilization of the CLC mixture, it has been demonstrated that the photo-addressable reflection of the notch can be switched on and off with an alternating-current (AC) voltage. The polymer-stabilized CLC with the novel combination of phototunability and electrically switchability is demonstrated in Figure 6. The original blue reflection can be turned on and off with an applied AC voltage. Subsequent exposure to UV light red-shifts the reflection color from blue to green. At this point, application of an AC voltage of 210 V also switches the reflection on and off.

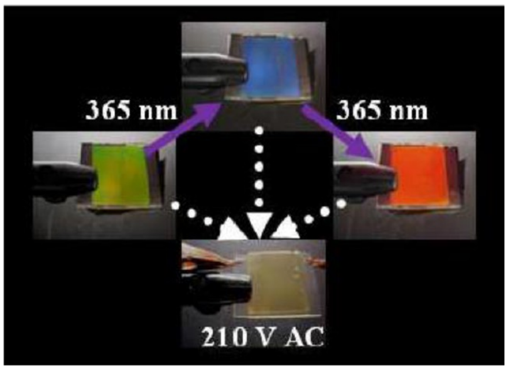


Figure 6. Demonstration of the phototuning and electric field switching of a polymer-stabilized CLC. Reproduced with permission from ref 26. Copyright 2010 Optical Society of America.

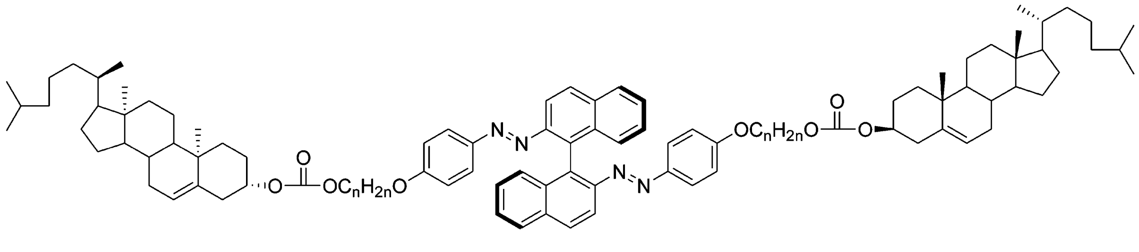
Azobenzene-based switches that possess both axial and tetrahedral chirality (Scheme 4) were also synthesized.[27] Light-driven chiral molecular switch **4a** doped into the LC host E31 at low concentration was found to be able to phototune the reflection color of the resulting CLC thin film over the visible region.

Subsequently, we combined the axially chiral binaphthyl unit with two mesogenic rodlike units through methyleneoxy linkers (Scheme 5).[28] Since the chemical structure of the rodlike cyclohexylphenyl moieties resembles that of the hosts, it was found that chiral switch **5a** has very good solubility in LC host E7 with an HTP of 304 μm^{-1}. This switch enabled the reversible tuning of the reflection color from the UV region to the NIR region by sequential irradiation with UV and visible light (Figure 7). Here an optically written and electrically controlled display device was made using switch **5a** (Figure 8), in which the optically written reflective image can be hidden in focal conic texture by the application of a 30 V pulse and reappears when a 60 V pulse is applied (Figure 8). Moreover, by the application of a 30 V pulse to an optically written image to make the UV-irradiated region go to the focal conic texture and the non-UV-irradiated region go to the planar texture, an optically written image can be stored indefinitely since the planar and focal conic textures are stable even though the light-driven switch relaxes to the nonirradiated state.

We designed cyclic azobenzenophanes **6** with axial chirality (Scheme 6), which showed high HTPs in three different LC hosts (E7, 5CB, and ZLI-1132).[29] These switches exhibited the unique capability to induce a reversible helix inversion in the cholesteric phase upon light irradiation (Figure 9), primarily because of the change in the dihedral angle between the naphthalene units. For example, the typical oily-streak texture observed in the CLC under planar alignment conditions was quickly transformed to a planar achiral nematic (N) texture upon irradiation with UV light (Figure 9a,b). This transient N phase was quickly transformed to a CLC phase upon continued UV irradiation for a few more seconds (Figure 9d). The helix inversion process was reversible with 440 nm irradiation.

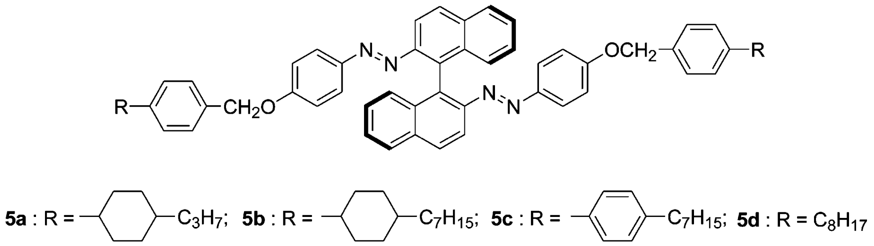
Light-directed dynamic red, green, and blue (RGB) color change would be a viable alternative to electrically directed color reflective displays. To examine the above possibility, we synthesized two new chiral molecular switches, **5b** and **5c**, that have very high HTPs and display significant differences in HTP in different states.[30] A visible-light-reflecting CLC was formulated by the addition of switch **5b** into LC E7. As a

Scheme 4. Chiral Molecular Switches 4 Possessing Both Axial and Tetrahedral Chirality



4a : n = 9; **4b** : n = 11

Scheme 5. Axially Chiral Azobenzene Molecular Switches 5



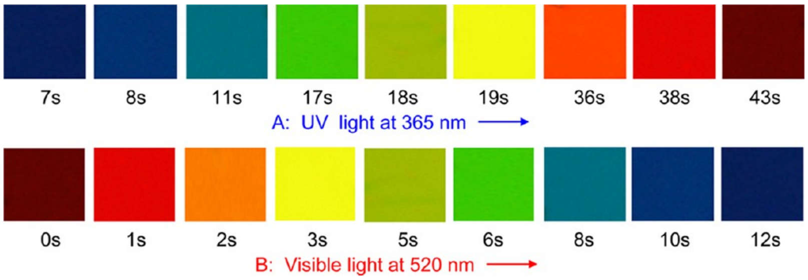


Figure 7. Light-driven reversible full range color tuning across the visible region and beyond. Reproduced with permission from ref 28. Copyright 2010 The Royal Society of Chemistry.

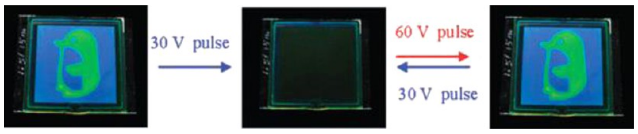
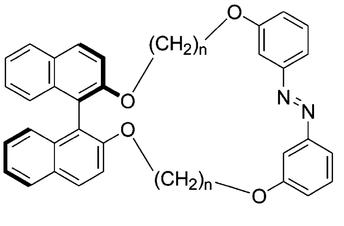


Figure 8. Images of optically written and electrically controlled color photodisplays. Reproduced with permission from ref 28. Copyright 2010 The Royal Society of Chemistry.

Scheme 6. Cyclic Chiral Azobenzene Molecular Switches 6



6a : n = 3, **6b** : n = 5

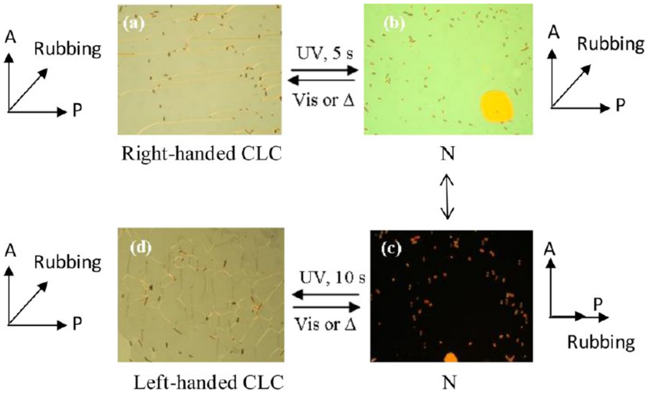


Figure 9. Demonstration of helix inversion in a CLC doped with cyclic azobenzene **6a**. Reproduced from ref 29. Copyright 2010 American Chemical Society.

result of the large change in HTP of the chiral molecular switch, dynamic RGB reflections can be obtained by UV and visible-light irradiation. Interestingly, photostationary state (PSS) RGB reflection colors were realized in the UV-pre-exposed CLC mixture upon exposure to visible light at 440, 450, and 550 nm, respectively. Thus, both dynamic and static RGB reflections were achieved in the CLC mixture. Moreover, a photo-addressable and multistimuli-switchable CLC display was demonstrated, as shown in Figure 10. "LCI" was written in the cell by photomasking under light irradiation at 365 nm (Figure 10A-iv). The reflectivity of the image in both the outside and photowritten areas disappears upon the application

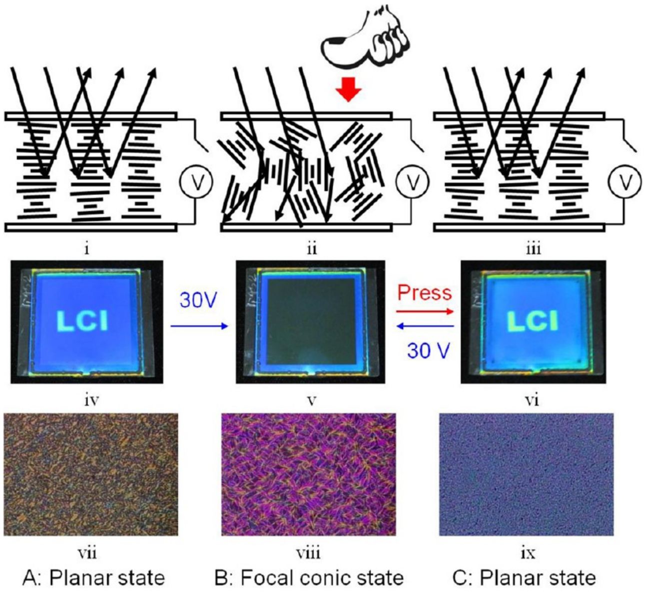


Figure 10. Light-, electric-field-, and mechanical-pressure-driven CLC color photodisplays: (top) schematic illustrations of cholesteric textures; (middle) demonstration of an image; (bottom) cross-polarized textures. Reproduced with permission from ref 30. Copyright 2011 Wiley-VCH Verlag GmbH & Co.

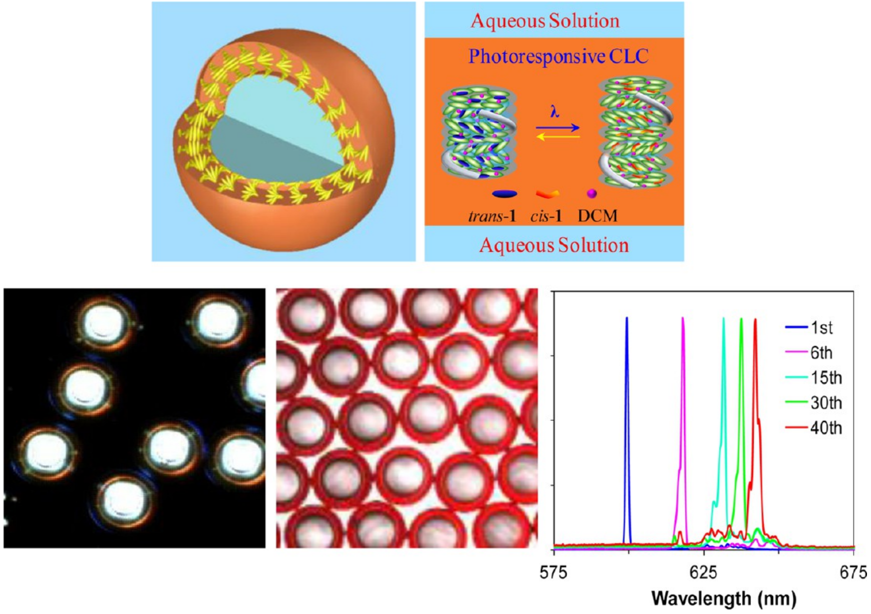


Figure 11. (top) Schematic illustrations of the structure of the photoresponsive monodisperse CLC microshell as a water–oil–water double emulsion (left) and the mechanism of phototunable lasing enabled by a light-driven chiral molecular switch (right). (bottom) Cross-polarized (left) and confocal (middle) images of the CLC microshells and phototuning of the laser emission (right). Reproduced with permission from ref 31. Copyright 2014 Wiley-VCH Verlag GmbH & Co.

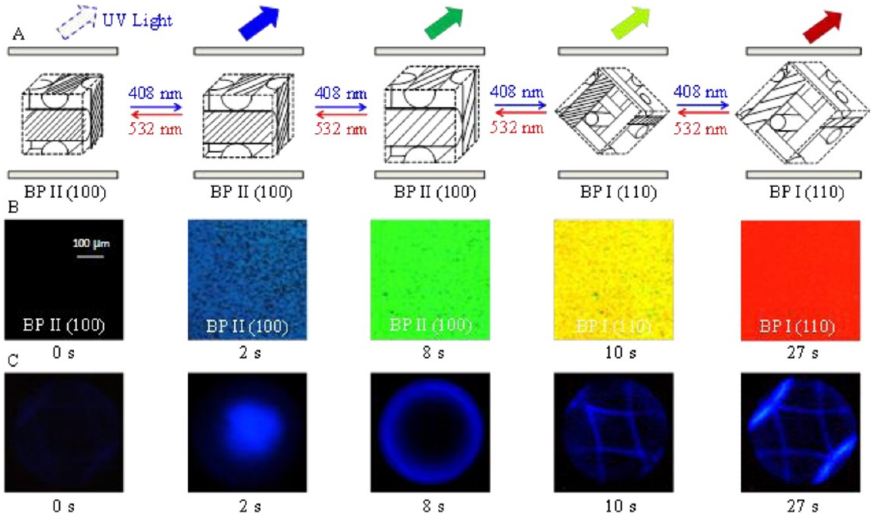


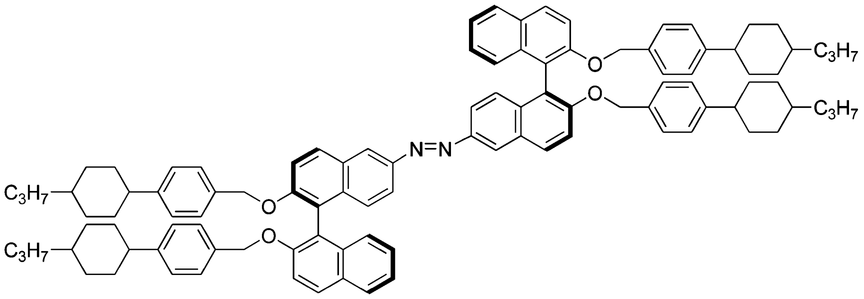
Figure 12. (A) Schematic illustration of the phototuning of the PBG in induced BPs. (B) Reflection images of a BP in a 7.5 μm thick planar cell upon irradiation with 408 nm light. (C) The corresponding Kossel diagrams. Reproduced with permission from ref 32. Copyright 2013 Wiley-VCH Verlag GmbH & Co.

of a 30 V electric pulse (Figure 10B-v). The hidden image can be restored simply by applying pressure (Figure 10C-vi).

We recently synthesized chiral molecular switch **5d** (Scheme 5), which undergoes green-light laser-induced photoisomerization.[31] From **5d**, a visible-light-responsive 1D CLC mixture and 3D monodisperse cholesteric microshells were fabricated. The resulting microshell droplets were water–oil–water double emulsions, in which the oil phase consisted of the photoresponsive CLC with a radial orientation of its helical axes. We demonstrated omnidirectional laser emission from the photoresponsive cholesteric microshells with the radial orientation of the helical axes within the shells by laser irradiation. The pumping laser light not only excited the laser dye but also concomitantly tuned the laser emission wavelength. Thus, upon repeated pumping, a red shift in the lasing peak wavelength was induced by photoisomerization of the chiral switch and the consequent shift in the PBG of the cholesteric microshells (Figure 11).[31]

Recently, LC BPs that self-organize into a 3D periodic cubic lattice have been recognized as soft self-assembled 3D photonic crystals. It should be noted that BPs exist in highly chiral LCs between the CLC and isotropic phases. If the 3D cubic lattice of the BP can be made photoresponsive, then it may be possible to tune the PBG of the BP and widen its scope as a 3D photonic crystal. To explore this possibility, we synthesized the chiral molecular switch **3d** (Scheme 3) and fabricated photoresponsive BPs.[32] The resulting BPs exhibited unprecedented reversible light-induced PBG tuning over the visible region across the RGB wavelengths (Figure 12). Such soft self-

Scheme 7. Visible-Light-Driven Axially Chiral Azobenzene Switches 7



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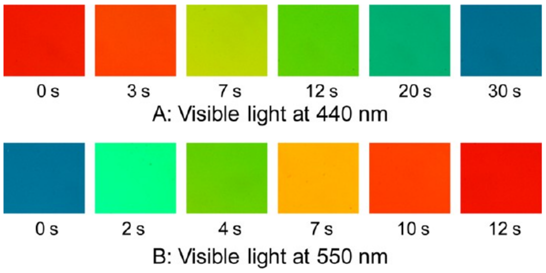
organized 3D photonic crystals could provide an exciting impetus for the development of all-optical device applications.

Because of the disadvantages of UV light, it is highly desirable to develop azobenzene-based chiral molecular switches that can undergo trans–cis isomerization upon visible-light irradiation. One way to achieve this goal is to extend the π conjugation of the aromatic groups linked to the azobenzene moiety. Keeping this in mind, we designed two enantiomeric azo molecular switches **7** with axial chirality (Scheme 7).[33] It was indeed found that these compounds with extended π conjugation undergo photoisomerization only upon visible-light irradiation. These chiral switches were able to induce an optically tunable helical superstructure in achiral NLCs. Moreover, reversible dynamic RGB reflections were achieved from the CLC mixtures by using only visible-light irradiation (Figure 13).[33]



A: Visible light at 440 nm

B: Visible light at 550 nm

Figure 13. Visible-light-driven reflection color tuning in CLC films. Reproduced from ref 33. Copyright 2012 American Chemical Society.

After the successful demonstration of pitch modulations of CLCs by UV and visible-light irradiation, we looked toward the possibility of reflection tuning by NIR irradiation. The idea is to exploit the obvious advantages of NIR light (superior penetration, less photodamage of materials, etc.) over UV and visible light. Thus, we turned our attention to upconversion nanoparticles (UCNPs), which are known to absorb NIR irradiation and emit UV and visible light. We synthesized a new azo switch (Figure 14) whose UV and visible absorptions significantly overlap with the emission of the $NaGdF_4$ UCNPs.[34] This switch and the core–shell UCNPs were mixed with an achiral LC. The resulting nanoparticle-impregnated CLC was found to exhibit reversible NIR-light-guided tunable behavior by simple modulation of the excitation power density of an NIR laser (980 nm). Upon irradiation by the NIR laser at high power density, the reflection wavelength of the photonic superstructure was red-shifted, whereas the reverse process occurred upon irradiation at lower power density (Figure 14).

Incorporating multiple chiral binaphthyl moieties with opposite absolute configurations into a single molecule functionalized with photoresponsive groups could be a novel route to generate materials capable of helix inversion, where the chiral conflict and equilibrium shifting between opposite chiral configurations in the molecular switch could promote the handedness inversion of the resulting helical superstructures upon light irradiation. Toward this end, an axially chiral azoarene unit with the *R* configuration was selected as the central scaffold and was laterally linked with two other binaphthyl units with either the *S* or *R* configuration. Accordingly, a series of molecular switches **8** (Scheme 8) were synthesized and investigated.[35] It was found that most of the switches were able to cause handedness inversion upon light irradiation of their CLC mixtures in different LC hosts. The optical observations of the handedness inversion and the proposed mechanism are depicted in Figures 15 and 16, respectively.

3. CHIRAL DITHIENYLCYCLOPENTENES IN LC NANOSTRUCTURES

Among photochromic compounds, dithienylcyclopentenes are particularly fascinating because of their superior thermal stability and excellent fatigue resistance. Upon irradiation with UV light, they can transform from a colorless open-ring form to a colored closed-ring form. The reverse process cannot be achieved thermally and occurs only by visible-light irradiation. Compared with chiral azobenzene switches, dithienylcyclopentenes possess the advantage of thermal irreversibility in both the open- and closed-ring isomeric states. However, only a few derivatives of dithienylcyclopentenes have been reported as chiral switches capable of inducing photoresponsive CLCs. Moreover, the reported chiral dithienylcyclopentenes exhibited low to moderate HTPs. These relatively low HTPs give rise to the requirement of higher doping concentrations, which often leads to phase separation and coloration and alters the desired physical properties of the LC host. Therefore, it would be of great practical interest to develop chiral dithienylcyclopentenes with high HTPs. Keeping this in view, we initiated a research program to design and synthesize novel dithienylcyclopentene-based chiral molecular switches with high HTPs. We began by synthesizing compounds **9** (Scheme 9). These photochromic CLCs contain one dithienylcyclopentene moiety linked to two well-known mesogenic cholesteryl groups via flexible carbonyldioxyalkoxy spacers.[36] When used as mesogenic chiral switches in an NLC, these photochromic switches induced photoresponsive CLCs. Figure 17 shows the induced CLC-to-isotropic phase transition and its reverse upon light irradiation.

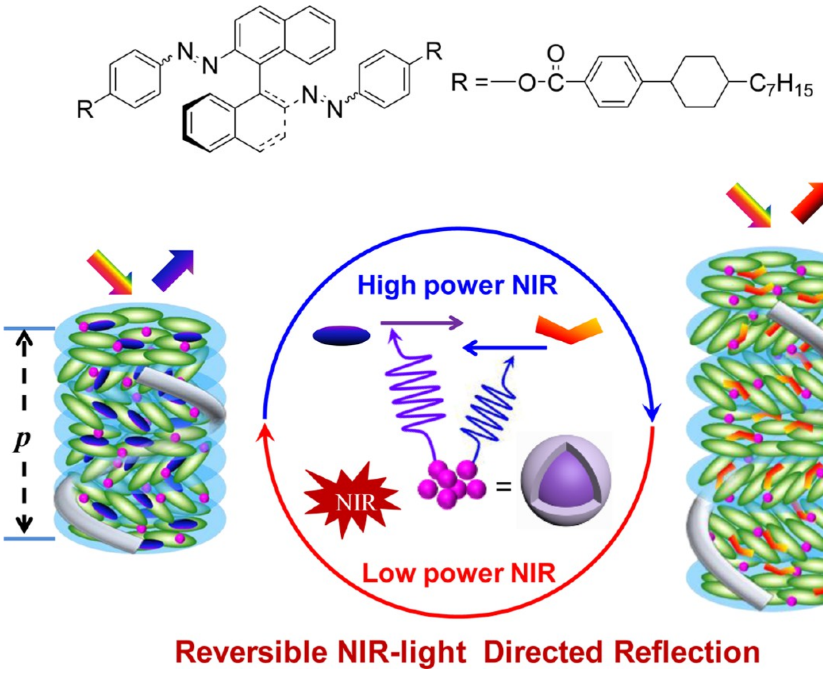
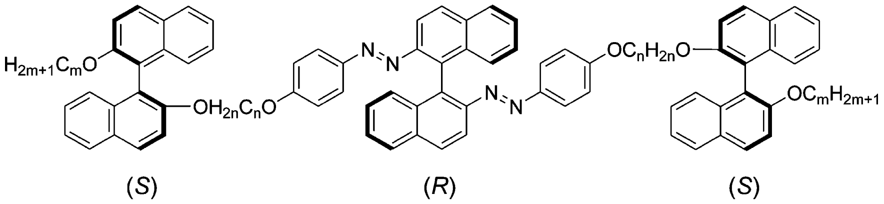


Figure 14. Upconversion-nanoparticle-doped reflection color tuning of CLCs. Reproduced from ref 34. Copyright 2014 American Chemical Society.

Scheme 8. Axially Chiral Azoarenes 8 Containing Binaphthyl Groups with Opposite Absolute Configurations



8a : m = 18, n = 11; **8b** : m = 8, n = 6; **8c** : m = 8, n = 3

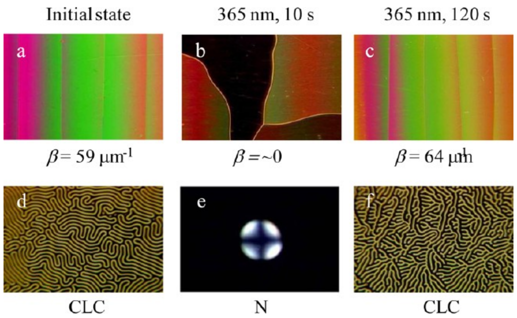


Figure 15. Illustration of helix inversion in (a–c) a wedge cell and (d–f) a homeotropic cell from (a, d) a right-handed CLC to (c, f) a left-handed CLC through (b, e) a transient nematic phase observed under cross-polarized optical microscopy. Reproduced with permission from ref 35. Copyright 2013 Wiley-VCH Verlag GmbH & Co.

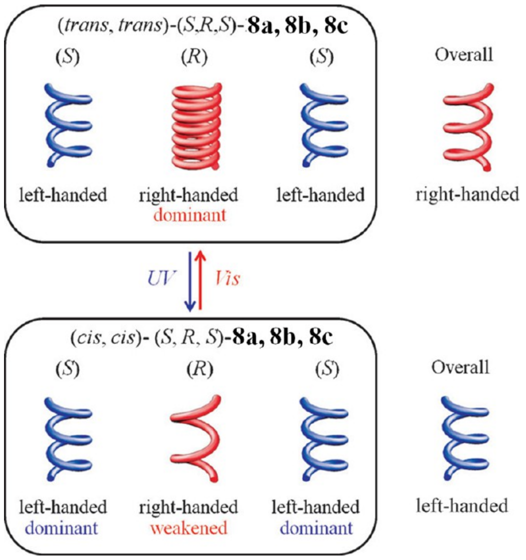
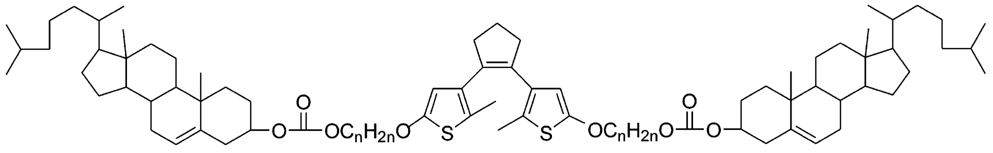


Figure 16. Schematic mechanism of helix inversion. Reproduced with permission from ref 35. Copyright 2013 Wiley-VCH Verlag GmbH & Co.

Encouraged by our results on axially chiral azobenzene switches, we decided to prepare axially chiral dithienylcyclopentenes by linking axially chiral binaphthyl units to photochromic dithienylcyclopentenes. Therefore, we designed and synthesized switches **10** and **11** (Scheme 10).[37] The design of these new chiral switches utilizes the combination of a photochromic dithienylcyclopentene core and two side chains, each containing an axially chiral binaphthyl unit. Molecular switches **10** exhibited unusually high HTPs, which were significantly higher than those of the known chiral diarylethenes reported previously.

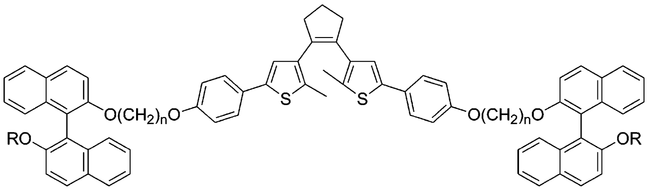
Scheme 9. Chiral Dithienylcyclopentene LCs 9



9a : n = 6; **9b** : n = 9; **9c** : n = 11

Figure 17. Photostimulated phase transitions in a CLC containing molecule **9a**. Reproduced from ref 36. Copyright 2011 American Chemical Society.

Scheme 10. Axially Chiral Diarylethenes 10 and 11

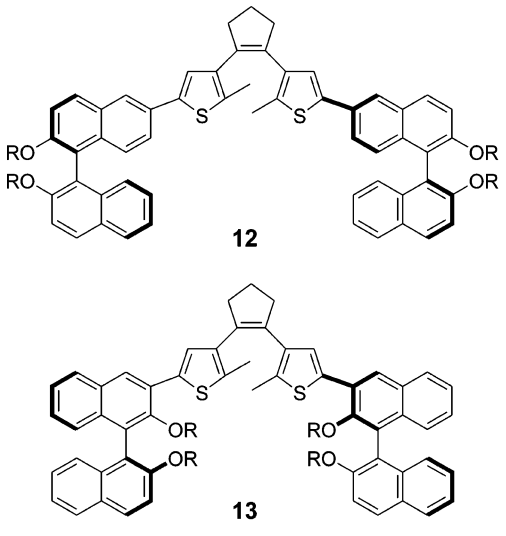


(S,S) or (R,R)-**10** : n = 6, R = C_8H_{17}

(S,S)-**11** : n = 11, R = —$(CH_2)_{11}$O—⟨⟩—⟨⟩—CN

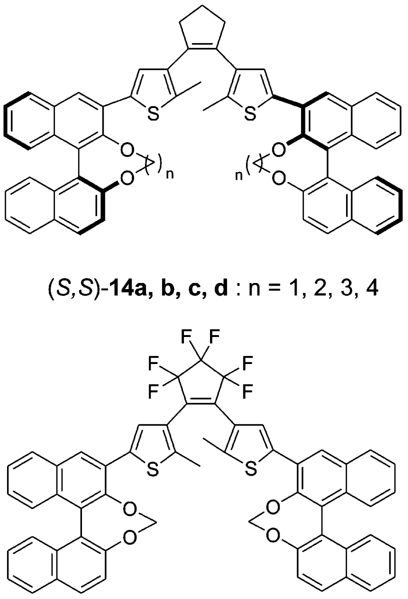
Subsequently, we linked chiral binaphthyl groups directly to the central dithienylcyclopentene unit using the Suzuki–Miyaura cross-coupling protocol.[38] In this work, we prepared two different series of axially chiral switches, **12** and **13**, by linking the binaphthyl groups to the dithienylcyclopentene unit through their 6 and 3 positions, respectively (Scheme 11). When doped into NLCs, these chiral molecular switches efficiently induced the cholesteric phase. It was found that compounds **12** possess very high HTP values in different NLCs. Although chiral switches **13** show lower HTP values than **12**, their changes in HTP are greater than those of **12**, enabling them to provide a wide range of tunability of the reflection wavelengths of CLCs.

Scheme 11. Axially Chiral Dithienylcyclopentenes 12 and 13. R is *n*-alkyl Chain



We recently synthesized the new series of chiral dithienylcyclopentene switches **14** (Scheme 12) by appending two bridged binaphthyl groups to the dithienylcyclopentene unit, with each member of the series having a different bridge length.[39,40] As anticipated, one of the members of the series, **14b**, exhibits the highest HTP value (228 μm^{-1}) among the diarylethene chiral dopants known to date.[40] Interestingly, the different members of the series with different alkylenedioxy bridges display unique characteristics with respect to their helicity induction capabilities in NLCs. Compound **14a** with a methylenedioxy bridge shows a remarkable increase in HTP upon UV irradiation, thus enabling a blue shift of the reflection color, whereas visible-light irradiation results in a red shift of the reflection color. Moreover, the three primary RGB colors could be demonstrated in a single thin film by varying the UV irradiation time while masking different areas of the CLC film (Figure 18). Compounds **14b** and **14c** exhibit much higher HTPs than **14a** but experience a dramatic decrease in HTP during photoisomerization that leads to a red shift of the reflection upon UV irradiation. Increasing the bridge length to butylenedioxy afforded compound **14d**, which possesses moderate HTPs in both states. Surprisingly, this compound

Scheme 12. Chiral Diarylethenes 14 and 15 Containing Bridged Binaphthyls with Different Bridge Lengths



(S,S)-**14a, b, c, d** : n = 1, 2, 3, 4

(S,S) or (R,R)-**15**

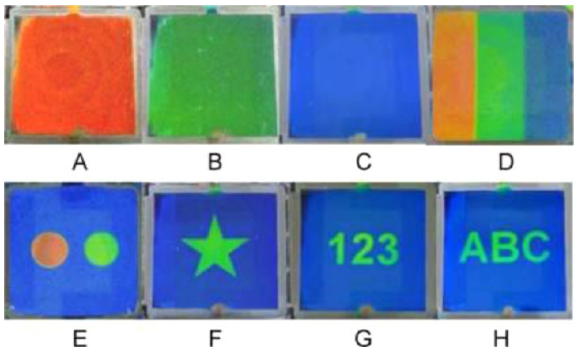


Figure 18. Thermally stable RGB reflection colors in CLC films containing **14a**. Reproduced from ref 39. Copyright 2012 American Chemical Society.

causes light-driven reversible handedness inversion of the CLCs fabricated from three different NLC hosts (E7, 5CB, and ZLI-1132) upon photoisomerization. Right-handed helices were induced in all of the hosts before UV irradiation, but upon UV irradiation the right-handed helices unwound, yielding nematic phases that upon further UV irradiation afforded left-handed helices, as observed by optical microscopy studies (Figure 19).

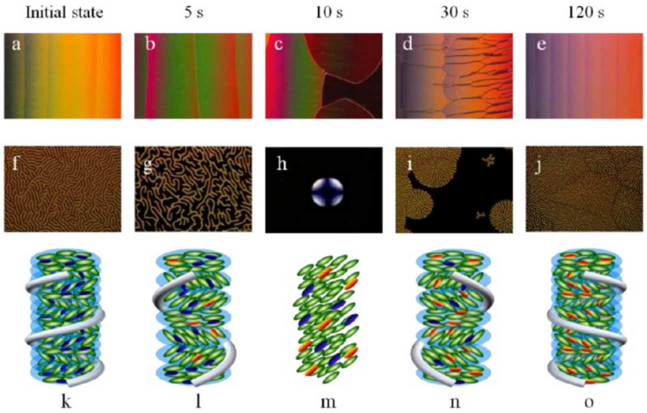


Figure 19. Demonstration of helix inversion in CLC films containing **14d** in (a–e) a wedge cell and (f–j) a homeotropic cell upon UV irradiation and (k–o) schematic illustrations of the corresponding LC phases. The inset in (h) shows a conoscopic observation. Reproduced with permission from ref 40. Copyright 2013 Wiley-VCH Verlag GmbH & Co.

To rationalize these observations, we analyzed the optimized geometries of the molecules in their open and closed forms by density functional theory calculations. Compound **14d** was found to exist in a cisoid conformation in its open form, which changes to a transoid conformation in its closed form upon light irradiation. This dihedral angle change explains the handedness inversion capability of chiral switch **14d**.

In continuation of our research on diarylethenes, very recently we reported chiral switch **15** containing a dithienyle-perfluorocyclopentene unit and two bridged binaphthyl groups (Scheme 12).[41] This switch with superior thermal stability was found to possess very high HTPs in different NLC hosts.

4. CHIRAL SPIROOXAZINES IN LC NANOSTRUCTURES

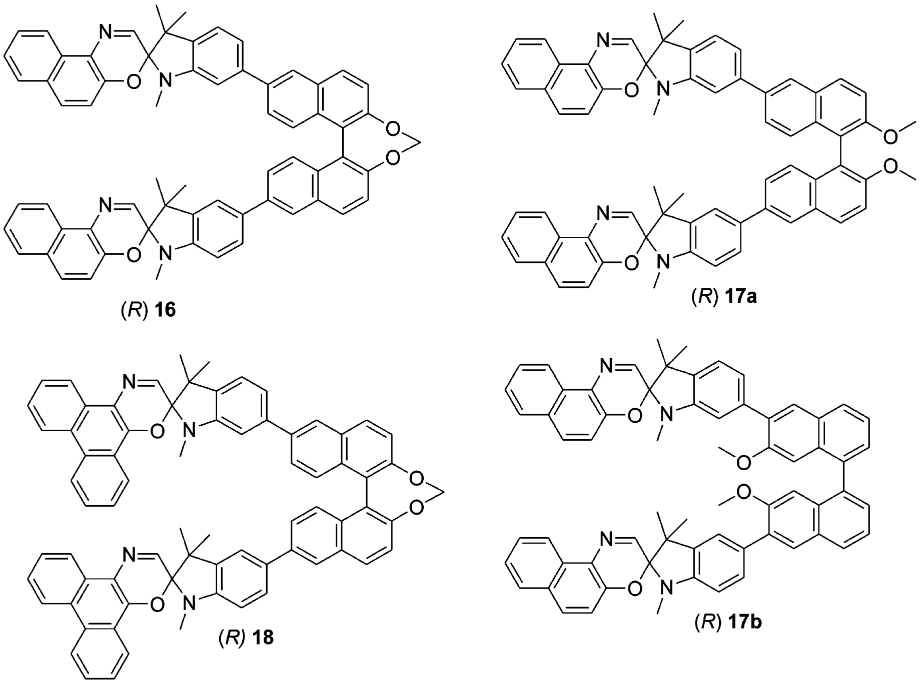
Spirooxazines are an interesting family of photoresponsive materials because of their promising properties such as photofatigue resistance, strong photochromism, and fast thermal relaxation. The colorless ring-closed spiro form of a spirooxazine can be transformed into the colored ring-opened merocyanine form upon UV irradiation, whereas the reverse process occurs thermally in the dark or photochemically by visible-light irradiation. The isomerization of the spirooxazine upon light irradiation can be used to control the helical pitch and photochromic behavior, which would open the door to many applications. However, there have been only very few reports on chiral spirooxazines. To tailor chiral spirooxazines with satisfactory functionalities, we designed and synthesized novel axially chiral spirooxazines **16**, **17**, and **18** (Scheme 13).[42] These switches were found to possess high HTPs. As expected, doping the spirooxazines into NLC hosts at low concentrations induced CLCs. It was noticed that the bridged chiral spirooxazines exhibited higher HTPs than the corresponding unbridged counterparts. Interestingly, for compounds **16** and **18**, the HTPs increase upon UV light irradiation, while the HTP of **17** decreases under the same conditions.

5. CONCLUSIONS AND PERSPECTIVES

In this brief Account, we have presented some of our new ideas and strategies for the design and synthesis of chiral molecular switches with exceptionally high HTPs and handedness inversion capabilities. The high HTP values have enabled the fabrication of photoresponsive CLCs by the addition of small quantities of the light-driven switches, thereby insignificantly affecting the optimized physical properties of the LC hosts. Large variation of the HTPs in different states of the switches allows phototuning of the selective reflection color (PBG) across the entire visible spectrum and beyond in cholesteric (1D) and BP (3D) photonic crystals. By appropriate molecular engineering and judicious choice of materials, UV-, visible-, and NIR-light-driven phototuning of the cholesteric pitch has been achieved. Dynamic and static RGB color reflections in a single film and photoaddessable optical displays without patterned electronics have been demonstrated as viable new technologies. Moreover, omnidirectional lasing with concomitant tuning of the laser emission wavelength has been shown in cholesteric microshells. Scarcely observed light-driven reversible helix inversion of cholesteric superstructures has been obtained by serendipity as well as by rational molecular design.

After 125 years of research on LCs, the study of CLC and BP systems still proves to be one of the most fascinating, fertile, and exciting areas for investigations and applications. Photoresponsive CLCs and BPs have turned from exotic systems to materials with interesting properties for a variety of applications. It is evident that the whole field is still a juvenile one and offers ample opportunity for molecular design and discovery. Thus, these mesophases have been and will likely continue to be of academic and technological importance. The modern view of CLCs and BPs as self-organized dynamic 1D and 3D photonic stop-band structures has opened up a multitude of potential applications that excite and inspire current interest. This Account is expected to provoke innovative ideas leading toward the design and engineering of new chiral molecules that may self-organize in predicted ways in order to produce materials that have desirable properties. Looking forward, the coupling of nanoparticles in LC films to enable synergistic performance attributes is becoming very active field that will undoubtedly extend into CLC and BP materials.[43] Incorporation of novel ways to impart patterned, hierarchically ordered structures will push this special class of

Scheme 13. Chiral Spirooxazine Molecular Switches 16, 17, and 18



intriguing color-generating materials into new and unimaginable applications.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: qli1@kent.edu.

Notes

The authors declare no competing financial interest.

Biographies

Hari Krishna Bisoyi is a postdoctoral research associate in the group of Prof. Quan Li at Kent State University. He received his Ph.D. (2010) from Jawaharlal Nehru University, working at the Raman Research Institute (India) under the guidance of Prof. Sandeep Kumar.

Quan Li is the Director of the Organic Synthesis and Advanced Materials Laboratory at the Liquid Crystal Institute at Kent State University, where he is also Adjunct Professor in the Chemical Physics Interdisciplinary Program. He has directed research projects supported by the NSF, DOE, AFOSR, AFRL, DoD-MURI, DoD-Army, NASA, the Ohio Third Frontier, and Samsung Electronics, among others. He received his Ph.D. in Organic Chemistry from the Chinese Academy of Sciences (CAS) in Shanghai, where he was promoted to be the youngest Full Professor of Organic Chemistry and Medicinal Chemistry in February 1998. He was a recipient of the CAS One-Hundred Talents Award (BeiRenJiHua) in 1999. He was Alexander von Humboldt Fellow in Germany. He has also won the Kent State University Outstanding Research and Scholarship Award.

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