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LIGHT-DRIVEN CHIRAL MOLECULAR MOTORS FOR PASSIVE AGILE FILTERS

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Final Report**

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FINAL REPORT

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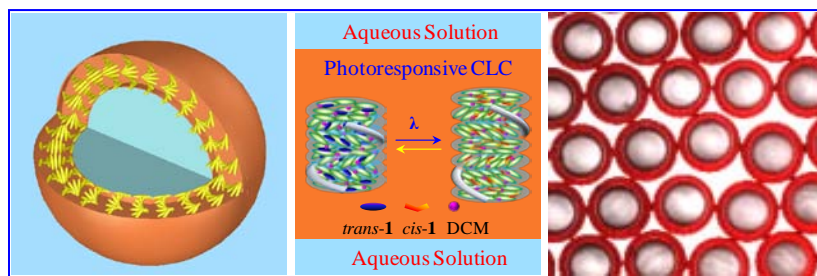
ABSTRACT (SUMMARY)

As we proposed originally, the major objective of this project was to synthesize novel light-driven chiral molecular motors or switches targeted specifically for the development of large tuning range, passive agile filters as counter-DE materials. Now this project has accomplished all the proposed objectives and beyond. The team led by PI Quan Li has conceptualized the design and synthesis, and characterized many novel functional light-driven chiral molecular motors or switches using the three widely used photochromic building blocks, *i.e.* azobenzene, dithienylethene and spirooxazine. The “world record” helical twisting power of the three different types of light-driven chiral molecular switches to date has been achieved due to this AFOSR funded project. Moreover, we have for the first time demonstrated the reversible tuning of reflection wavelength of the self-organized helical superstructure across the entire visible spectrum enabled by UV-visible light, visible-visible light, and the near-IR light with the change of power intensity; light-directing reversible handedness inversion of helical superstructures with and without thermal relaxation was accomplished enabled by the novel light-driven chiral molecular switches; and unprecedented reversible light-directed red, green and blue reflections of the self-organized three-dimensional cubic nanostructure in a single film were demonstrated for the first time. Furthermore, from the photoresponsive one-dimensional helical superstructure, we have for the first time fabricated the phototunable three-dimensional monodisperse micro-shell photonic superstructure through a capillary-based microfluidic method and demonstrated omnidirectional laser emission. In close collaboration with the groups in Air Force Research Laboratory at Wright-Patterson Air Force Base, this project has turned out to be a game-changer in creating innovative well-defined nanostructured materials for the next generation of counter-DE agile filters, acting as smart materials that autonomously respond to a given stimulus without the need of bulky, power-draining, and heavy electronics, and has opened new avenues with tremendous opportunities and challenges for further exploration. This project has led to about 21 journal publications in which 15 papers are coauthored with the collaborators at AFRL [9 papers with impact factor over 10 which are *Adv. Mater.*, *Angew. Chem. Int. Ed.*, and *J. Am. Chem. Soc.*, and two papers highlighted two times by Nature Photonics as “research highlights” (Nature Photonics 2011, 5, 713) and “News & Views” (Nature Photonics 2013, 7, 767)], and 10 book chapters and encyclopedia entry.

Accomplishments/New Findings

1. **Photoresponsive Monodisperse Cholesteric Liquid Crystalline Micro-Shells for Tunable Omnidirectional Lasing Enabled by a Visible Light-Driven Chiral Molecular Switch** (*Advanced Optical Materials* **2014**, 2, DOI: 10.1002/adom.201400166).

The ability to construct self-organized three-dimensional (3D) superstructures with desired



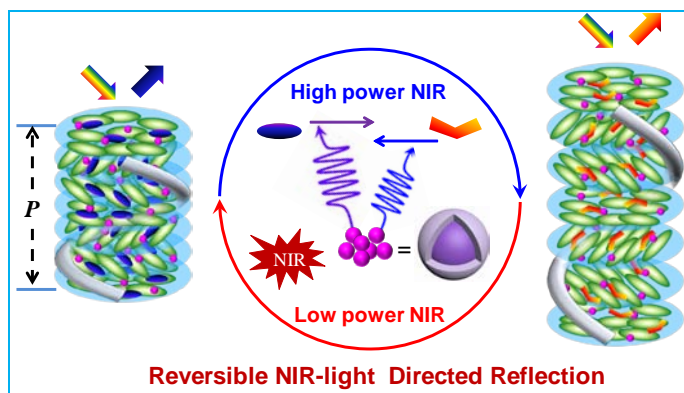
functionality is not only of scientific significance but also crucial in the bottom-up nanofabrication of smart molecular devices. Very recently, in a close collaboration with Prof. David Weitz at Harvard University,

we custom designed and synthesized a new visible light-driven chiral molecular switch and

developed a photoresponsive one-dimensional (1D) cholesteric liquid crystal employing the molecular switch. From the photoresponsive 1D liquid crystal, we fabricated the self-organized, phototunable 3D photonic superstructure, *i.e.* photoresponsive monodisperse cholesteric liquid crystalline micro-shells, through a capillary-based microfluidic method. The resulting monodisperse micro-shell droplets were water-oil-water double emulsions, in which the oil phase consisted of the photoresponsive cholesteric liquid crystal with radial orientation of its helical axes. The cholesteric microshells exhibited band-edge lasing in all directions, and the wavelength of the resultant photonic band edge laser was reversibly tuned by the pumping laser causing photoisomerization of the chiral molecular switch.

2. Reversible Near-Infrared Light Directed Reflection in a Self-organized Helical Superstructure Loaded with Upconversion Nanoparticles (*Journal of the American Chemical Society* **2014**, *136*, 4480-4483)

Adding external, dynamic control to self-organized superstructures with desired functionalities is an important leap necessary in leveraging the fascinating molecular systems for applications.



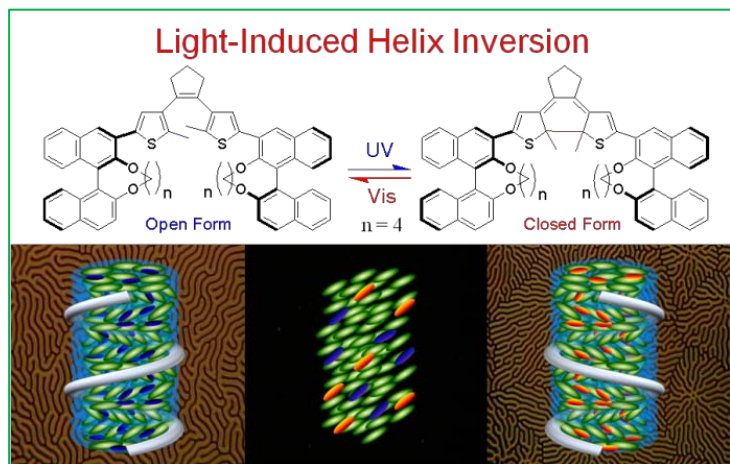
Here the new light-driven chiral molecular switch and upconversion nanoparticles, doped in a liquid crystal media, were able to self-organize into an optically tunable helical superstructure. The resulting nanoparticle impregnated helical superstructure was found to exhibit unprecedented reversible near-infrared (NIR) light guided tunable behavior only by modulating the excitation power density of a continuous-

wave NIR laser (980 nm). Upon irradiation by the NIR laser at the high power density, the reflection wavelength of the photonic superstructure red-shifted, whereas its reverse process occurred upon irradiation by the same laser but with the lower power density. Furthermore, reversible dynamic NIR-light driven red, green and blue reflections in a single thin film, achieved only by varying the power density of the NIR light, were for the first time demonstrated. The concept disclosed and demonstrated here offers a convenient and versatile method to spatially and temporally regulate the self-organized helical photonic superstructures and their dynamic reflections. This study also shows that synergetic effects of appropriate materials combinations can yield functional materials with applicable properties.

2. Photodynamic Chiral Molecular Switches with Thermal Stability: From Reflection Wavelength Tuning to Handedness Inversion of Self-Organized Helical Superstructures (*Angewandte Chemie International Edition* **2013**, *52*, 13703-13707).

The ability to tune and control self-organized superstructures with desired properties using an external stimulus is a major driving force in the bottom-up nanofabrication of intelligent molecular devices. Light-driven chiral molecular switches or motors in liquid crystal (LC) media that are capable of self-organizing into an optically tunable helical superstructure, namely photoresponsive cholesteric LCs (CLCs), are such striking examples. The most important property of CLCs is the selective reflection of circularly polarized light (CPL): When unpolarized light propagates through the CLC medium, only CPL with the same handedness as

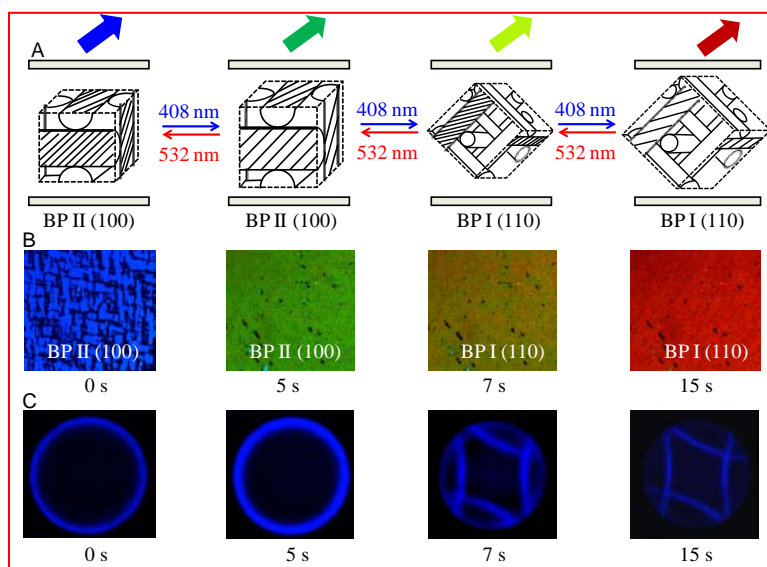
the helix is reflected, and the reflection wavelength can be determined by $\lambda = nP$, where n is the average refractive index of the LC medium. The light induced pitch change and the resulting reflection wavelength tuning of CLCs have found widespread applications in color filters and reflectors, tunable lasers, and reflection displays that require no driving electronics and can be flexible. Furthermore, the ability to control the chirality of CLCs with a helix inversion in response to light holds great potential for the development of stimuli-responsive materials for



technological applications in areas where CPL is involved. Here three new dithienylethene compounds bearing two axially chiral bridged binaphthyl units with different bridge lengths were synthesized and employed as photodynamic chiral doants for nematic LCs. They exhibited different intriguing properties depending on the bridge length. The dopant with ethylene bridged-binaphthyls showed unusually high helical twisting powers (HTPs) in both states, which are significantly

larger than those of the known chiral diarylethene dopants so far. More interestingly, with the increase of bridge-length from ethylenedioxy to butylenedioxy, the dihedral angel in these dopants can be modulated to switch the binaphthyl units from *cisoid* form to *transoid* form, which led to the handedness inversion of induced self-organized helical superstructure in different liquid crystals with moderate to high HTPs at both states.

3. Red, Green and Blue Reflections Enabled in Optically Tunable Self-Organized 3D Cubic Nanostructured Thin Film (*Advanced Materials* 2013, 25, 5050-5054, highlighted in *Nature Photonics* 2013, 7, 767).



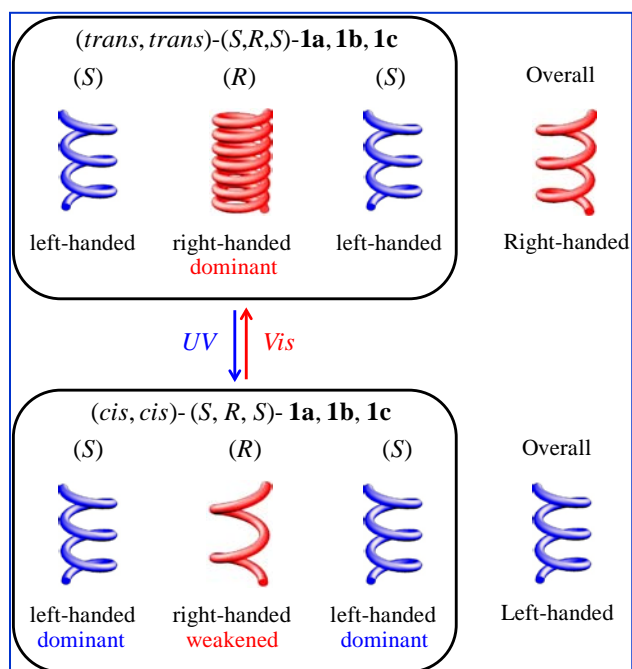
The ability to tune self-organized nanostructures with tailored properties using an external stimulus is a driving force in the bottom-up nanofabrication of functional smart materials. Light-driven molecular switches or motors capable of self-organizing the host liquid crystal media into an optically tunable three-dimensional cubic nanostructure, *i.e.* optically tunable blue phase, undoubtedly represents an elegant example due to its unique property of photonic band gap selective reflection of incident light and its

consequent application potentials. Here a new light-driven axially chiral molecular switch doped

in a stable blue phase liquid crystal was found to endow wide optical tunability of the three-dimensional cubic nanostructure whose selective reflection wavelength was reversibly tuned through the entire visible region. Moreover, unprecedented reversible light-directed red, green and blue reflections of the self-organized three-dimensional cubic nanostructure in a single film were demonstrated for the first time. Additionally, unusual isothermal photo-stimulated less ordered BP II to more ordered BP I phase transition was observed in the system. Such soft self-organized 3D photonic crystals provide an exciting impetus for developing light-driven chiral molecular switches or motors with tailored properties for all-optical device applications.

4. Azoarenes Bearing Opposite Chiral Configurations: Light-Driven Dynamic Reversible Handedness Inversion in Self-Organized Helical Superstructure (*Angewandte Chemie International Edition* **2013**, *52*, 8925-8929, Hot paper selected by the editors for the importance in a rapidly evolving field of high current interest).

Stimuli directing self-organized supramolecular architectures with tailored functionalities have proved extremely fascinating for the creation of intelligent molecular devices. Light-driven helicity induction and handedness inversions in self-organized helical superstructures, *i.e.*

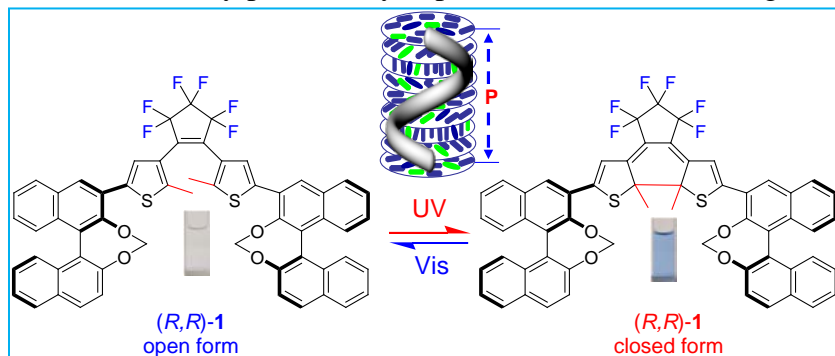


cholesteric liquid crystals (CLCs) represent an elegant example because of their unique property of selective reflection of circularly polarized light (CPL) and light wielding advantages of remote, spatial, and temporal controllability. Such systems might be achieved by doping photoresponsive chiral molecules into an achiral nematic liquid crystal (LC) host to self-organize into an optically tunable helical superstructure. However, to date, the photoresponsive chiral dopants capable of inducing light-driven handedness inversions in self-organized helical superstructures mainly depend on chance, *i.e.* it is not designable and predictable for a photoresponsive chiral molecule to have the ability to induce handedness inversion driven by light. A series of azoarene compounds containing axially

chiral moieties with different chiral configurations were designed and synthesized. The chiral conflict and equilibrium shifting between opposite chiral configurations in these compounds was utilized to promote the handedness inversion of the resulting helical superstructures. It is found that their handedness inversion can be realized in different LC hosts and the HTPs at both states are moderate to high. The design strategy can be realized by simply changing the terminal chains and spacer lengths in these molecules to understand the structure property relationships. The strategy demonstrated here would provide new and exciting insights into developing photoresponsive liquid crystal materials for practical applications and further stimulate rational design of handedness inversion materials.

5. Photoswitchable but Thermally Stable Axially Chiral Dithienylperfluorocyclopentene Dopant with High Helical Twisting Power (*Journal of Materials Chemistry C* **2013**, *1*, 3889-4044, highlighted on the front cover and selected as hot article).

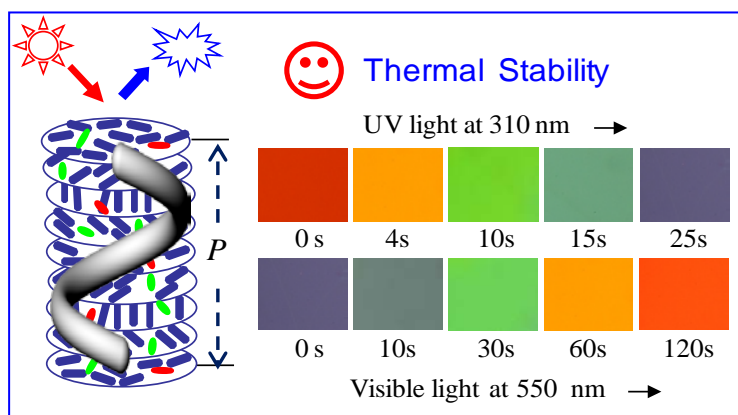
A chiral dithienylperfluorocyclopentene molecule bearing two bridged binaphthyl units was designed and synthesized by a Suzuki-Miyaura cross-coupling reaction between chiral binaphthyl iodide and dithienylperfluorocyclopentene e-derived bis(boronic ester). Its photoresponsive properties were investigated in both organic solvent and liquid crystal media. The UV-vis



spectra exhibited typical photochromic changes of diarylethenes upon UV irradiation. The CD spectra changes upon light irradiation indicated that the conformation of binaphthyl unit and the chiroptical properties of this molecule could be modulated by light. More importantly, when using as chiral dopant in nematic liquid crystals, this molecule could induce cholesteric liquid crystals with very high helical twisting powers. At very low doping concentration, this dopant was able to induce a reversible isothermal phase transition between nematic and cholesteric phases upon light irradiation. The photochemical control of the pitch length of cholesteric phases at higher doping concentrations enabled the reversible reflection wavelength control in the visible region. Superior thermal stability and excellent fatigue resistance were also observed during photoswitching process, which are important properties for applications. The high HTPs combined with excellent thermal stability and fatigue resistance are believed to be helpful for the development of more powerful molecular switches and represents progress towards practical applications.

6. Reversible Light-Directed Red, Green and Blue Reflections with Thermal Stability Enabled by a Self-Organized Helical Superstructure (*Journal of the American Chemical Society* **2012**, *134*, 9573-9576).

Controlling the dynamic nature of molecular self-organization with an external stimulus is a challenge in science and technology that, when overcome, could lead to a breakthrough in the creation of new intelligent molecular devices. Here two novel light-driven dithienylethene chiral molecular switches possessing remarkable changes in helical twisting power during photoisomerization as well as very high helical twisting powers were found to experience photochemically reversible isomerization with thermal stability in both isotropic organic solvents and anisotropic liquid crystal media.

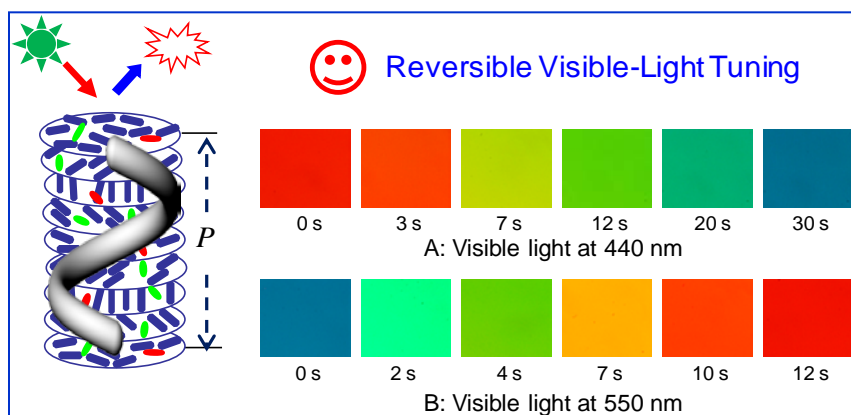


When doped into a commercially available achiral liquid crystal host, the chiral switch was able

to either immediately induce an optically tunable helical superstructure or retain an achiral photoresponsive liquid crystal phase whose helical superstructure was induced and tuned reversibly upon light irradiation. Moreover, reversible light-directed red, green and blue reflection colors with thermal stability in a single thin film were demonstrated. Of significance are the superior thermal stability and excellent fatigue resistance of the light-directing tuning of self-organized helical superstructure in a controllable way, which are important for practical applications.

7. Reversible Visible-Light Tuning of Self-Organized Helical Superstructures Enabled by Unprecedented Light-Driven Axially Chiral Molecular Switches (*Journal of the American Chemical Society* **2012**, *134*, 3342-3345).

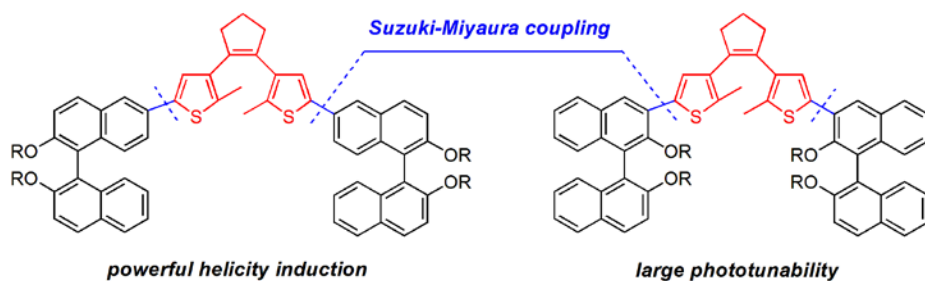
The ability to tune molecular self-organization with an external stimulus is a main driving force in the bottom-up nanofabrication of molecular devices. Here, two enantiomeric light-driven azo molecular switches, with axial chirality and extended conjugation, were found to exhibit unprecedented reversible photoisomerization in both organic solvent and liquid crystal media



only upon visible-light irradiation. The chiral switch, doped in an achiral liquid crystal with different concentration, was able to either immediately induce an optically tunable helical superstructure or still retain achiral liquid crystal phase whose helical superstructure was induced and tuned reversibly upon visiblelight

irradiation. Furthermore, reversible dynamic red, green and blue reflection, achieved only by using visible light, was demonstrated. This new family of chiral azo dopants and the visible-light driven transitions provide an exciting impetus for developing light-driven chiral molecular switches or motors with enhanced functionalities for practical device applications.

8. Photochemically Reversible and Thermally State Axially Chiral Diarylethene Switches (*Organic Letters* **2012**, *14*, 4362-4365).



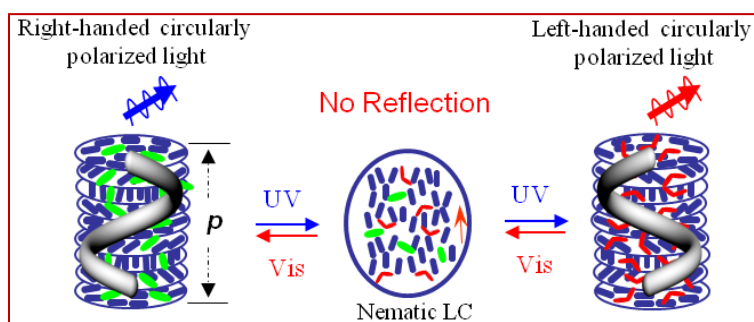
A series of novel photochemically reversible and thermally stable dithienylcyclopentene switches containing two axially chiral binaphthyl units were designed and synthesized. The

Suzuki-Miyaura coupling between binaphthyl-derived halides with diboronate ester gave the products with good yields. Their photoswitching properties were characterized in both organic

solvents and LC media. Furthermore, their cholesteric induction behavior was found to be dependent on the incorporation style of binaphthyl units. Attachment of binaphthyl through 6-position generated very high HTP compounds, among which (*S,S*)-**4a** was successfully employed to tune the reflection color in the visible range. When the binaphthyl units were introduced through the 3-position, the products show significant changes of HTP during photoisomerization. Compound (*S,S*)-**4f** was found to be capable of reversibly switching the LC phase between nematic and cholesteric. The novel structures, high HTPs, as well as the interplay between structure and chiroptical properties would provide impetus towards developing more powerful diarylethene switches for practical applications.

9. Light-Driven Chiral Molecular Switches or Motors in Liquid Crystals (*Advanced Materials* **2012**, *24*, 1926-1945).

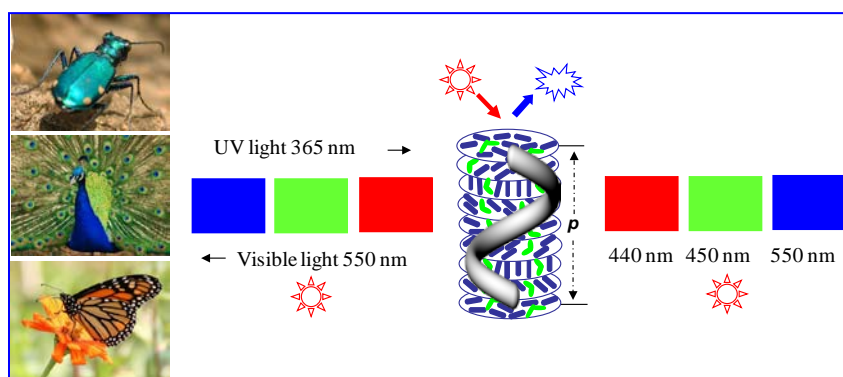
The ability to tune molecular self-organization with an external stimulus is a main driving force in the bottom-up nanofabrication of molecular devices. Light-driven chiral molecular switch or



motor in liquid crystal capable of self-organizing into optically tunable helical superstructures undoubtedly represent such a striking example owing to their unique property of selective reflection of light and its consequent potential applications. In this review, we focus on different classes of light-driven chiral

molecular switches or motors in liquid crystal media for the induction and manipulation of photoresponsive cholesteric liquid crystal system and their consequent applications. Moreover, the change of helical twisting powers of chiral dopants and their capability of helix inversion in the induced cholesteric phases are highlighted and discussed in the light of their molecular geometric changes.

10. Directing Dynamic Control of Red, Green and Blue Reflection Enabled by a Light-Driven Self-Organized Helical Superstructure (*Advanced Materials* **2011**, *23*, 5069-5073, Highlighted in *Nature Photonics* **2011**, *5*, 713).



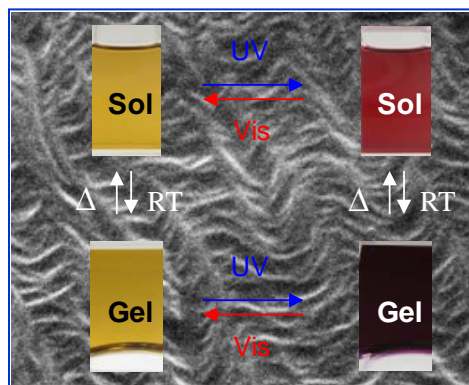
Color abounds in nature. Often times, the color is based on structure rather than pigments, observed in the elegant colors of butterfly wings, bird feathers, and beetle exoskeletons. Recent examinations of iridescent beetles correlate their brilliant color patterns to a structure reminiscent of the

cholesteric liquid crystal (LC) phase. As a subset of structural color, the helical superstructure of

cholesteric LC exhibits vibrant colors by selectively reflecting circularly polarized light according to Bragg's law. Here, two new light-driven chiral molecular switches possessing very high helical twisting powers were introduced into an achiral liquid crystal host at low doping concentrations enabling a self-organized, helical superstructure whose properties could be dynamically and reversibly controlled with light. Light exposure enabled fast and reversible tuning of the selective reflection color from blue to red. Variation of the irradiation wavelengths also enabled realization of photo-stationary states of red, green and blue reflection colors. Marrying reflection wavelength to the wavelength of irradiation offers a distinctive and novel means to simultaneously achieve red, green and blue reflection colors in a single optical thin film. Photoaddressing of the material system allows for images to be retained, which are hidden with an applied electrical field and restored by application of a mechanical field.

11. **Self-Organized Photochromic Dithienylcyclopentent Organogels** (*Journal of Materials Chemistry* **2011**, *21*, 15673-15677).

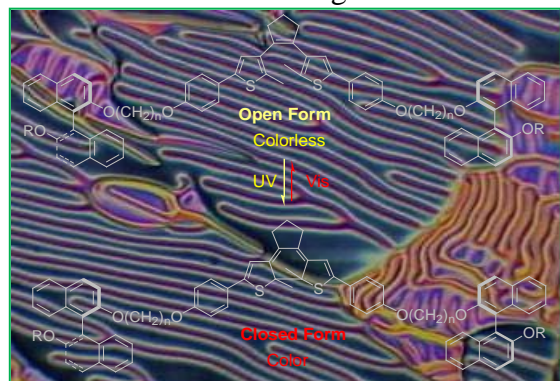
Organogelators, *i.e.* functional materials that assemble to macroscopic three-dimensional (3D) networks and immobilize organic solvent molecules in the networks, recently have emerged as a class of fascinating self-organized materials. Self-organization of organogelator molecules acting as low molecular weight gelators (LMWGs) into an entangled supramolecular 3D fibrous network in organic solvents is often driven by weak intermolecular interactions such as electrostatic, dipole-dipole, hydrogen bonding and π - π interactions. Any variation of the molecular structure of organogelators would affect the corresponding intermolecular interactions, and hence the morphology and properties of the resulting gels. In this context, smart molecular materials, consisting of small molecules responsive to external stimuli, may provide a promising route towards active control over the properties and multi-scale structures of organogels. Here four photochromic dithienylcyclopentene amides with a phenylene unit as a bridge between the amide and long alkyl chain, the first of their kind, were synthesized and characterized. They were found to be able to self-



organize into reversible photochromic organogels in apolar solvents. SEM and optical microscopy studies of their xerogels showed the typical fibrous networks. Temperature dependence of the sol-gel transition using shear rheology were evaluated. FT-IR, ^1H NMR, and fluorescence emission spectra indicate that such fibrous network might result from the cooperation of the hydrogen bonding between the amide groups and the π - π interactions between the aromatic moieties. These materials exhibited excellent reversible photochromism in both solution and gel states. The findings that hydrogen bonded networks enhanced by π - π interactions through the insertion of a phenylene bridge between the terminal alkyl chain and the center dithienylcyclopentene core would provide insight to design organogels with enhancement of gelation behavior.

12. **Synthesis and Characterization of Light-Driven Dithienylcyclopentene Switches with Axial Chirality** (*Journal of Organic Chemistry* **2011**, *76*, 7148-7156).

Self-organizing chiral liquid crystal (LC) architectures with phototunable properties have proved extremely fascinating for the design and fabrication of functional devices. Here three dithienylcyclopentene derivatives (*S,S*-**1a**, (*R,R*)-**1b** and (*S,S*)-**2** containing two axially chiral binaphthyl units were designed and synthesized. Their photoswitchable properties were characterized in both organic solvents and LC hosts. Upon irradiation with UV light, their

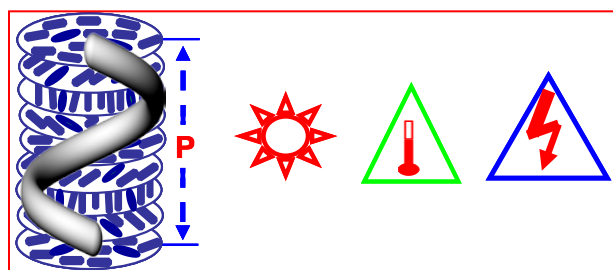


solutions in organic solvents changed from colorless to bright red, the irradiated or photostationary state is thermally stable and can be switched back by visible light irradiation. Doping them into an achiral LC host can efficiently induce the formation of a cholesteric phase. Of note is the unusually high HTP of (*S,S*)-**1a** or its enantiomer (*R,R*)-**1b**, which is significantly larger than the HTPs previously reported for chiral diarylethenes. The chiral molecular switch (*S,S*)-**1a** induced a left-handed cholesteric phase whereas its enantiomer

(*R,R*)-**1b** induced a right-handed cholesteric phase. Furthermore, the HTPs can be reversibly controlled by irradiation with UV light and visible light. The high HTP, photochemically reversible process with thermal stability, and excellent fatigue resistant properties would provide new and exciting insights into developing light-driven chiral molecular switches for practical applications.

13. Thermally, Photochemically and Electrically Switchable Reflection Colors from Self-Organized Chiral Bent-core Liquid Crystals (*Journal of Materials Chemistry* **2011**, *21*, 2098-2103).

The interplay between molecular structure and chirality has proved extremely fascinating for the design of various functional molecular assemblies. Intensive work has focused on chiral liquid crystal (LC) molecules which self-organize into various technologically important mesophase structures such as cholesteric (N^*), ferroelectric/antiferroelectric smectic phases and blue phases. In most cases, the chiral phases are obtained by tethering chiral units covalently to the conventional rod-, disc-shaped or polymeric mesogenic molecules.

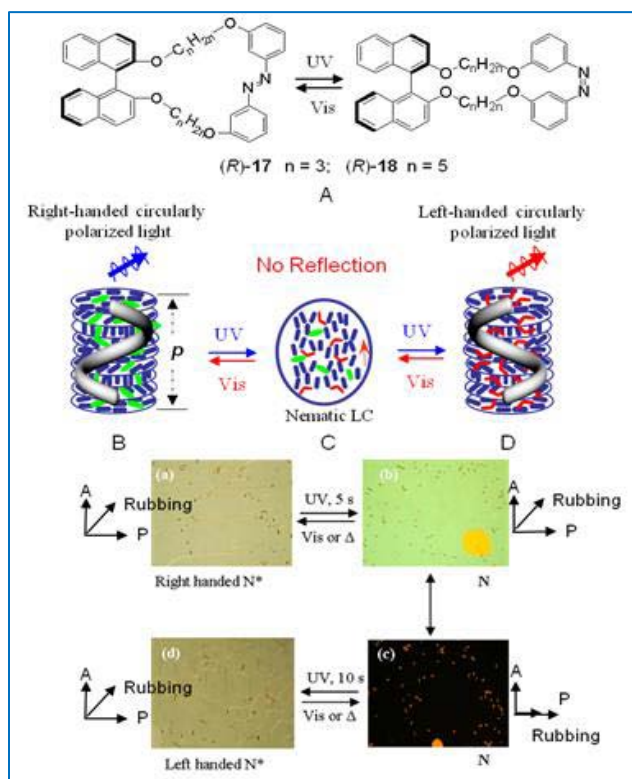


Alternatively, a chiral dopant dissolved in an achiral LC phase can also induce chiral mesophases. A notable exception is seen in mesophases of achiral bent-core (banana-shaped) LCs where the steric packing of molecules leads to polar order and chiral conformational states though the molecules are achiral. Although a large number of structurally different bent-core mesogens have been reported to date, only a few of them possess inherent chirality within their molecular structure. LCs that combine the unique electro-optic characteristics of bent-core molecules with chiral properties are interesting from the view point of molecular design for multifunctional materials. Here we report the synthesis and characterization of two new chiral 1,3-phenylene based five ring bent-core mesogens that combine the unique electro-optic characteristics of banana-shaped molecules with chiroptic properties. The two compounds reported here are the first examples of chiral

bent-core mesogens that stabilize exclusively the N* mesophase over a wide temperature range. Smectic mesophases predominantly seen in bent-core mesogens were completely suppressed in these molecules due to the steric intermolecular interactions arising from unsymmetrical nature of the molecules. The reflection colors from the cholesteric phase were reversibly tunable by external stimuli such as temperature, light and electric field. The mechanism for red shift in reflection band by changing temperature (upon cooling) or by UV irradiation is postulated on the basis of a cybotactic smectic clusters formed or destroyed in the cholesteric phase. Electric field induced blue shift in reflection band is attributed to the field induced tilting of the cholesteric helix leading to a shortening of the pitch. These findings are of significant importance for the design of new low molecular weight multi-stimuli responsive cholesteric materials with full range tunable reflection colors at ambient temperatures for reflective display applications and for full color recording media. Considering the shape biaxiality of the bent-core molecules and wide range stabilization of the cholesteric mesophase, we see these mesogens as potential candidates for the *hitherto* unknown thermotropic biaxial chiral nematic phase and the characterization studies in this direction are currently in progress.

14. Light-Driven Reversible Handedness Inversion in Self-organized Helical Superstructures (*Journal of the American Chemical Society* 2010, 132, 18361-18366).

Self-organization of chiral molecules into reversibly tunable helical systems with amplified chiral properties is a rapidly growing scientific area of contemporary interest. Cholesteric liquid



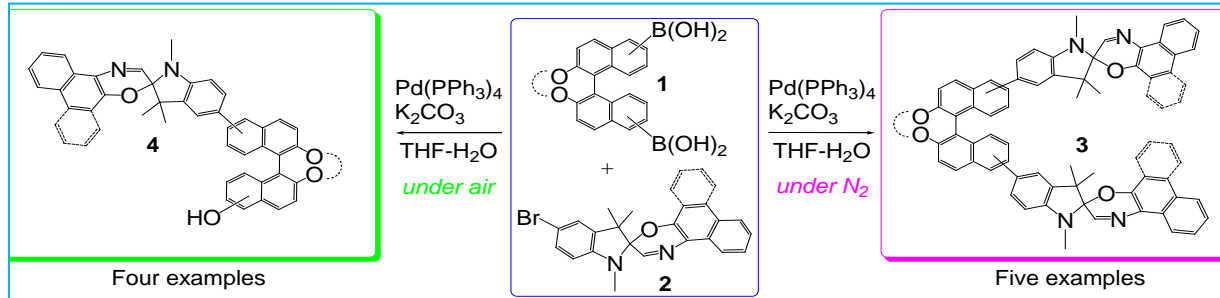
crystal phase is one such self-organized system. The circularly polarized nature of the reflected light is another remarkable property associated with CLCs. When unpolarized light impinges on the CLC material, circularly polarized light with the same handedness as the helix is reflected.² Circularly polarized light with the opposite handedness transmits through the sample. Outside the reflection band, incident light is transmitted regardless of its polarization state. Selective preparation of right-handed or left-handed CLC films is achieved from intrinsically chiral LC molecules or LC mixtures containing chiral dopants. Enantiomers of a chiral mesogen or chiral dopant are used to obtain an equal but opposite twist in the cholesteric phase. On the other hand, switching of the cholesteric helicity with external stimuli such as temperature, light or electric field can significantly improve and/or widen the area of potential applications of CLC materials.

Compared to the large body of literature describing the tunability of the cholesteric pitch to obtain red, green and blue reflection colors, a reversible switching of the cholesteric handedness by external stimuli such as temperature and light remains a challenging task. Here two cyclic

azobenzenophanes with axial chirality employed as phototunable chiral dopants were found to be able to induce helical superstructure in three structurally different achiral LC hosts and reversibly control the selective reflection colors from blue to near IR. More importantly, the different switching states of the light-driven chiral cyclic dopants (*i.e.* *trans-cis* isomerization) were capable of inducing a helical handedness inversion in the induced self-organized helical superstructures. Therefore, we could obtain a rapid change in the sign of the helical handedness by alternating UV and visible light irradiations. Fast switching (few seconds) of the handedness combined with tunability of the reflection colors over the entire visible range by light irradiation opens new perspectives for future applications. Furthermore, a new method was developed to allow us to directly determine the handedness of the long pitched self-organized helical superstructure.

15. Synthesis of Novel Thermally Reversible Photochromic Axially Chiral Spirooxazines (*Organic Letters* **2010**, *12*, 3552-3555).

Photochromic molecules, that change color upon irradiation with UV light, have attracted a great deal of interest because of their potential applications as smart light-driven molecular switches and devices. Among all the photochromic molecules, spirooxazines are a particularly interesting family due to their unique properties such as excellent photo-fatigue resistance, strong photo-coloration and fast thermal relaxation. The colorless ring-closed spiro form of spirooxazine can be transformed into the colored ring-opened merocyanine form upon irradiation with UV light whereas its reverse process occurs thermally in the dark or photochemically by irradiation with visible light. Since the physical and chemical properties of the two forms are dramatically different, the thermally reversible photochromic switching has been the basis for the intelligent

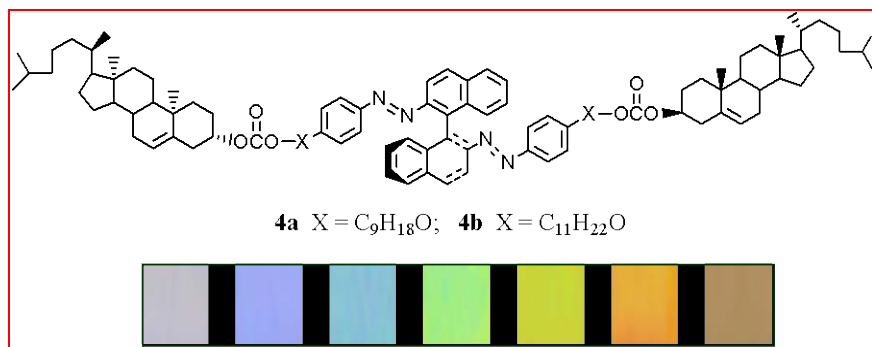


materials with applications in three-dimensional optical memory, photochemical erasable memory, self-developing photography, actinometry, displays, filters, lenses of variable optical density and photoswitchable sensors. However, to date, there have been only very few reports on chiral spirooxazines, compared with numerous other chiral photoresponsive molecules such as chiral azobenzenes, chiral dithienylethenes, chiral spiropyrans and chiral fulgides. Here a series of spirooxazines containing an axially chiral binaphthalene moiety, for the first of their kind, were synthesized and characterized. The Suzuki coupling reactions under N_2 atmosphere and aerobic condition gave the di-spirooxazine substituted binaphthyl product and the mono-spirooxazine substituted binaphthyl derivative, respectively. Both the ring-opening process upon irradiation with UV light and the thermally reversible ring-closing process were fast. The thermal relaxation rate is strongly influenced by the medium polarity as well as the structure of the spirooxazine. Furthermore, these axially chiral spirooxazines were found to impart their chirality to an achiral LC host, at low doping levels, to form a self-organized optically tunable helical superstructure. This bifunctional system is promising for future application because the system

exhibits excellent thermally reversible photochromic behavior and chiral induction capability in liquid crystal hosts.

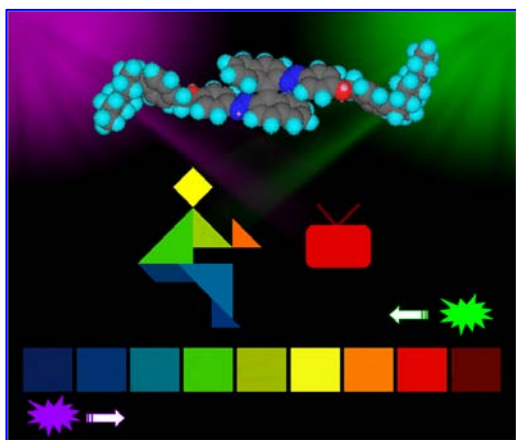
16. Light-Driven Nanoscale Chiral Molecular Switch: Reversible Dynamic Full Range Color Phototuning (*Chemical Communications* **2010**, 46, 3463-3465, Top ten download paper, and highlights in Chemical Technology).

The elegance of nature performing light-driven functions is inspiring scientists to develop intelligent molecular switches or motors for artificial nanomachines. Compared with the molecular switches driven by electric field, heat, chemical reaction or electrochemical reaction, those capable of being driven by light wield advantages of ease of addressability, fast response time and potential for remote control in a wide range of ambient environments. A major challenge is not only how to control the mechanical motion of molecules by light, but also how to transform such motion into a macroscopic change in a system. A promising solution lies in doping light-driven chiral molecules into liquid crystal (LC) media. Here a novel light-driven nanoscale chiral molecular switch with high helical twisting power that can reversibly phototune the reflection color across the full visible spectrum is presented. This chiral molecular switch was found to impart its chirality to a commercial LC host, at low doping levels, to form a self-organized, optically tunable helical superstructure capable



of fast and reversible phototuning of the structural reflection across entire visible region. To the best of our knowledge, this is the first report on reversible phototuning reflection color truly across entire visible region by employing light-driven

chiral molecular switch or motor as the only chiral dopant in a LC media. Reversible, dynamic, full range color tuning was able to be achieved in seconds just by light. Furthermore, this chiral switch was used in a color, photo-addressed liquid crystal display driven by light and hidden as well as fixed by application of an electric field from thermal degradation. The results provide new and exciting insights into developing light-driven chiral



molecular switches or motors for practical applications.

17. Light-Driven Chiral Molecular Switches with Tetrahedral and Axial Chirality [*Organic & Biomolecular Chemistry* (communications) **2009**, 7, 3930-3933].

The elegance with which nature use performs light-driven functions is inspiring chemists to develop smart light-driven molecular motors and switches for artificial molecular devices. An important challenge is to how to dynamically control mechanical motions of

molecules by light. A promising solution lies in the photoswitchable chiral nematic (cholesteric) phase because its 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. Here two novel light-driven chiral molecular switches with tetrahedral and axial chirality were synthesized, which can effectively induce chirality of achiral nematic host even at a low dopant concentration to form the so-called cholesteric liquid crystalline superstructure. Their reversible photoresponsive properties were well demonstrated. The material **4a** doped in achiral liquid crystal host E31 was found capable of being tuned the reflection color by light over the entire visible region. This research would provide new insight on developing light-driven chiral motors with satisfactory functionalities for device applications.

Publications during Reporting Period with Acknowledgements to the AFOSR Grant

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Synergistic Activities and Honors Which greatly benefited from the Project

- 2014 Kent State University Outstanding Research and Scholarship Award
- Invited Speaker at 2014 International Liquid Crystal Conference, Dublin.
- International Advisory Committee Member and Plenary Speaker at 2014 International Conference on New Energy and Sustainable Development, Beijing.
- The editor of the Springer book entitled *Nanoscience with Liquid Crystals: From Self-organized Nanostructures to Applications*, Springer, **2014** (ISBN 978-3-319-04866-6).
- The editor of the book entitled *Intelligent Stimuli-Responsive Materials: From Well-defined Nanostructures to Applications*, John Wiley & Sons, **2013** (ISBN 978-1-118-45200-4).
- The editor of the book *Liquid Crystals Beyond Displays: Chemistry, Physics, and Applications*, John Wiley & Sons, **2012** (ISBN 978-1-118-07861-7).
- The editor of the book entitled *Self-Organized Organic Semiconductors: From Materials to Device Applications*, John Wiley & Sons, **2011** (ISBN 978-0-470-55973-4).
- The invited author of the entry entitled "Liquid Crystals" for the prestigious *Kirk-Othmer Encyclopedia*, John Wiley & Sons (appear in 2014 Edition).
- Chair Session "Physical Organic Chemistry" at 2013 ACS National Fall Meeting at Indianapolis.
- 2013 Invited Speaker at 2013 Gordon Research Conference on Liquid Crystals; Chair Two Sessions "Materials, Device, and Switches" and "Gold Nanoparticles: Stabilization, Assembly, and Application" at 2012 ACS National Fall Meeting at Philadelphia.
- Invited Speaker at 2012 Symposium on Soft Matter Science, Georgia Tech, Atlanta.
- Advisory Committee Member and Plenary Speaker at Liquid Crystal Photonics 2012, Guilin.
- International Scientific Committee Member and Invited Speaker at 2011 International Conference on Smart Materials and Nanotechnology in Engineering, Shenzhen.
- International Advisory Committee Member and Plenary Speaker at 2011 International Symposium on Liquid Crystals: Science and Technology, Changzhou.
- Invited Speaker at Pacificchem 2010 Congress, Hawaii.

- Invited Speaker at 2010 LCOPV Workshop on Direct Nanoscale Self-organization in Organic Photovoltaics: Liquid Crystals for Energy, Boulder, Colorado.
- Invited Speaker at 2010 Complex Interactions and Mechanisms in Organic Photovoltaics Workshop in Brisbane.
- International Scientific Advisory Committee Member and Plenary Speaker at 2010 International Conference on Optical, Electronic and Electrical Materials, Kuming.
- Chair of Electroactive Polymer Session, Chair of Functional Materials Session, and Invited Speaker at 2009 International Conference on Smart Materials and Nanotechnology in Engineering, Weihai.
- Interviewed by *Materials Views* on October 18, 2011 at <http://www.materialsviews.com/materialsviews-interviews-quan-li/>
- Served as an active panelist/reviewer for funding agencies such as DOE, DoD, NSF, ACS PRF, Swiss NSF, and Chile National Fund and many publishing houses.