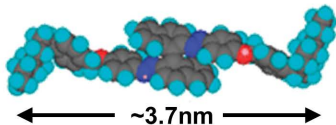
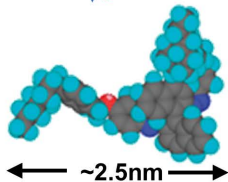
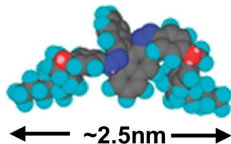
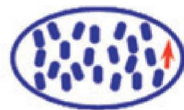
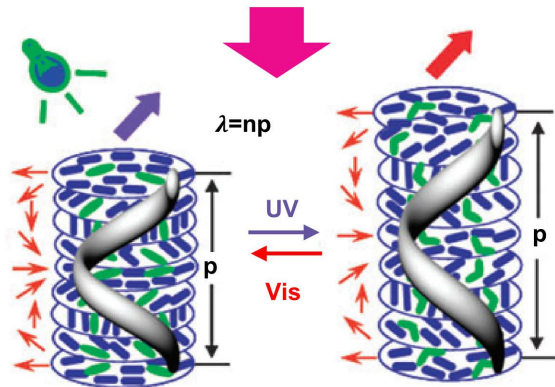


a**(trans,trans)-4** $\text{UV} \downarrow \uparrow \text{Vis or } \Delta$ **(trans,cis)-4** $\text{UV} \downarrow \uparrow \text{Vis or } \Delta$ **(cis,cis)-4****b**

Liquid Crystal

+

Light-driven
Chiral Switch



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Order License ID	1270861-1	Publisher	ROYAL SOCIETY OF CHEMISTRY
ISSN	1364-548X	Portion	Chart/graph/table/figure

LICENSED CONTENT

Publication Title	Chemical communications	Rightsholder	Royal Society of Chemistry
Article Title	Light-driven nanoscale chiral molecular switch: reversible dynamic full range color phototuning.	Publication Type	e-Journal
		Start Page	3463
		End Page	3465
Author/Editor	Royal Society of Chemistry (Great Britain)	Issue	20
		Volume	46
Date	01/01/1996		
Language	English		
Country	United Kingdom of Great Britain and Northern Ireland		

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Portion Type	Chart/graph/table/figure	Distribution	Worldwide
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Duration of Use	Current edition and up to 5 years	Incidental promotional use?	No
Lifetime Unit Quantity	Up to 499	Currency	USD
Rights Requested	Main product		

NEW WORK DETAILS

Title	Advanced liquid crystal-based switchable optical devices for light protection application: principles and strategies	Publisher imprint	N/A
		Expected publication date	2022-11-23
		Expected size (number of pages)	50
Author	Ruicong Zhang, Jiajun li, Zhibo Zhang, Jiecai Han, Lei Yang, Tianyu Wang, Jiaqi Zhu	Standard identifier	N/A

Publication	Light: Science & Applications
Publisher	Springer Nature

ADDITIONAL DETAILS

Order reference number	N/A	The requesting person / organization to appear on the license	Ruicong Zhang
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REUSE CONTENT DETAILS

Title, description or numeric reference of the portion(s)	Figure1, Figure 3	Title of the article/chapter the portion is from	Light-driven nanoscale chiral molecular switch: reversible dynamic full range color phototuning.
Editor of portion(s)	Ma, Ji; Li, Yannian; White, Timothy; Urbas, Augustine; Li, Quan	Author of portion(s)	Ma, Ji; Li, Yannian; White, Timothy; Urbas, Augustine; Li, Quan
Volume of serial or monograph	46	Issue, if republishing an article from a serial	20
Page or page range of portion	3463-3465	Publication date of portion	2010-05-28

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Light-driven nanoscale chiral molecular switch: reversible dynamic full range color phototuning†

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A light-driven nanoscale chiral molecular switch was found to impart its chirality to an achiral liquid crystal host to form a self-organized, optically tunable helical superstructure capable of fast and reversible phototuning of the structural reflection across the entire visible region.

The elegance of nature performing light-driven functions is inspiring scientists to develop intelligent molecular switches or motors for artificial nanomachines.¹ 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.² 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. Such systems can self-organize into unique optically tunable helical superstructures that are induced by the dopant chirality and possess the photoresponsive property of a light-driven chiral switch molecule (Fig. 1).^{3,4} The resultant chiral helical superstructure, *i.e.* cholesteric LC phase, can selectively reflect light according to Bragg's law and has the useful property of being tuned by light. 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 LC material.

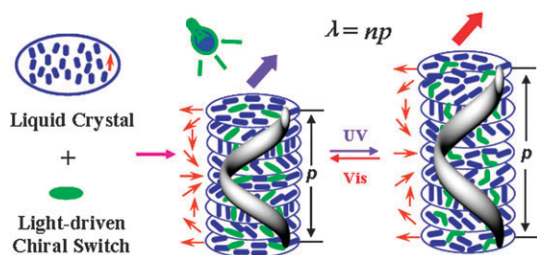


Fig. 1 A schematic mechanism of the reflective wavelength of a light-driven chiral molecular switch in an achiral nematic LC medium reversibly dynamically tuned by light.

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† Electronic supplementary information (ESI) available: Experimental details, synthesis, photoresponsive experiments, measurement of HTP, color driven by light, and measure of reflection response to a pulse. See DOI: 10.1039/c002436h

The ability of a chiral dopant to twist an achiral nematic LC phase, *i.e.* helical twisting power (HTP, β), is expressed in the equation: $\beta = (pc)^{-1}$ where c is the chiral dopant concentration. The isomerization upon light irradiation can control the HTP and reflection wavelength λ of the cholesteric phase, providing opportunities as well as challenges in fundamental science that are opening the door for many applications such as tunable color filters, tunable LC lasers, and optically addressed displays that require no drive electronics and can be made flexible.^{5–7} It is known that dynamic control of a change in color is a key feature of modern information technology. It is highly desirable to dynamically phototune the reflection color over the entire visible spectrum with only small amounts of light-driven chiral switch since a high concentration of chiral dopant can often lead to phase separation, coloration, and alter the desired physical properties of the LC host. This requires the dopant to have high HTP as well as a significant difference in HTP among the various states of the switch. To date full range color control in induced chiral nematic LC without added non-photoresponsive chiral co-dopants was limited to the recent reports such as using helically chiral overcrowded alkenes,^{8,9} planar chiral azobenzenophanes,¹⁰ axially chiral binaphthyl azobenzenes^{4,6} and binaphthyl azobenzenes with axial and tetrahedral chirality.¹¹ However, in most of these reports, the color change is either irreversible,⁸ or requires a relatively long thermal relaxation.^{4,6,9} Still other systems need a high concentration of planar chiral azobenzenophanes (12 wt%) or binaphthyl azobenzenes with axial and tetrahedral chirality (15 wt%) in which case the two systems are not fully covering the entire visible spectrum upon visible light irradiation.^{10,11} Undoubtedly, the discovery of new light-driven chiral molecular switches which exhibit good device performance at low doping concentrations, *e.g.* fast and reversible phototuning of the structural reflection over the entire visible spectrum, is important to their practical applications. Here we report a novel light-driven nanoscale chiral molecular switch **4** (Fig. 2) which meets the above satisfactory requirements.

The chiral molecular switch **4** was prepared in a facile synthesis. Its chemical structure was well identified by ¹H NMR, ¹³C NMR, high resolution MS and elemental analysis (see supporting information†). The material is chemically and thermally stable, and exhibits the expected fast

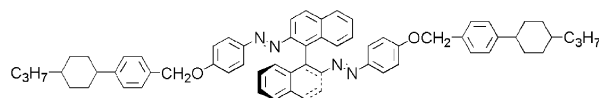


Fig. 2 Molecular structure of chiral molecular switch **4**.

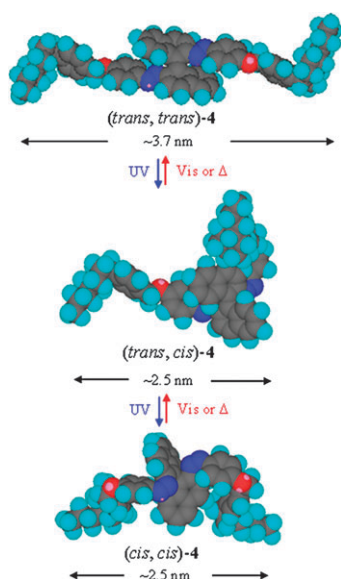


Fig. 3 *Trans*–*cis* isomerization of light-driven nanoscale chiral molecular switch **4** (3D-ChemDraw space filling model).

reversible optically tunable behavior in both organic solvent and LC media. For example, dark incubation of a solution of **4** in CH_2Cl_2 served to maximize the absorption at 354 nm corresponding to the (*trans*, *trans*)-azobenzene chromophore. Irradiation of this solution with 365 nm light resulted in clean photoisomerization to (*cis*, *cis*)-**4**, as evidenced by a decrease in the absorbance at 354 nm and an increase in the absorbance at 458 nm (see supporting information Fig. S2†). Due to the molecular switch having two azo linkages, UV irradiation leads to reversible *trans*–*cis* isomerization of azo configurations producing two other isomers containing one or two *cis* configurations, respectively. The sequence of the photochemical switch of the three isomers is (*trans*, *trans*)-**4** → (*trans*, *cis*)-**4** → (*cis*, *cis*)-**4**. The reverse process from (*cis*, *cis*)-**4** → (*trans*, *cis*)-**4** → (*trans*, *trans*)-**4** can occur thermally or photochemically with visible light irradiation (Fig. 3).

As expected, doping the chiral molecular switch **4** in an achiral nematic LC host even at a low concentration can induce an optically tunable helical superstructure, *i.e.* cholesteric phase, as evidenced by a characteristic oily streak texture. Their helical twisting powers were measured by using the Grandjean–Cano method.¹² Of significance is the unusually high HTP value at its initial state and a considerable difference in HTP among the various states the chiral switch exhibits (Table 1).

A mixture of 6.5 wt% **4** in LC medium E7 was capillary-filled into a 5 μm thick glass cell with a polyimide alignment layer and the cell was painted black on one side. Surprisingly, the wavelength of reflection light of the cell was able to be tuned starting from the UV region across the entire visible

Table 1 Helical twisting powers (β) of chiral molecular switch **4** at initial state and photostationary state (PSS) upon light irradiation in nematic E7

β (molar%) μm^{-1}			β (wt%) μm^{-1}		
Initial	PSS _{UV}	PSS _{VIS}	Initial	PSS _{UV}	PSS _{VIS}
304	89	198	90	26	58

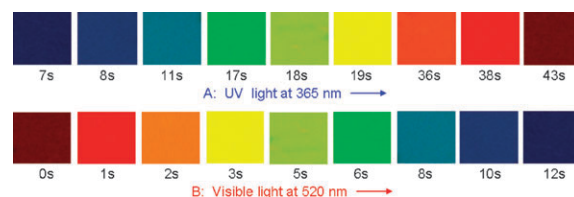


Fig. 4 Reflection color images of 6.5 wt% chiral switch **4** in commercially available achiral LC host E7 in a 5 μm thick planar cell. A: upon UV light at 365 nm (5.0 mW cm^{-2}) with different times; B: reversible back across the entire visible spectrum upon visible light at 520 nm (1.5 mW cm^{-2}) with different times. The colors were taken from a polarized reflective mode microscope.

region to the near infrared region upon UV irradiation at 365 nm (5.0 mW cm^{-2}) within approximately 50 s. Its reversible process starting from the near infrared region across the entire visible region to the UV region was achieved by visible light at 520 nm or dark thermal relaxation. The reflection colors were uniform and brilliant (Fig. 4A and B). The reversible process with visible light is much faster than dark thermal relaxation. For instance, the phototuning time of 6.5 wt% **4** in E7 with a visible light irradiation at 520 nm (1.5 mW cm^{-2}) from the near IR region back across the entire visible region to the UV region is within 20 s (Fig. 5 bottom) whereas its dark thermal relaxation back through the entire visible region took approximately 10 h (see supporting information Fig. S6†). Each reflection spectrum (Fig. 5) has no drawback such as the dramatic change of the peak intensity and bandwidth compared with electric field-induced color tuning.¹³ The reversible phototuning process was repeated many times without degradation. It is worth noting here that the reversible phototuning process across the entire visible region was able to be achieved in seconds with the increase of light exposure intensity (see supporting information Fig. S7†).

Compared with our previous reported axially chiral molecules,^{6,11} the ability of chiral molecular switch **4** to quickly and reversibly phototune the reflection color over the entire visible region may result from the introduction of the mesogenic low-molecular-weight rod-like cyclohexylphenyl building block. This could induce a more dramatic geometrical

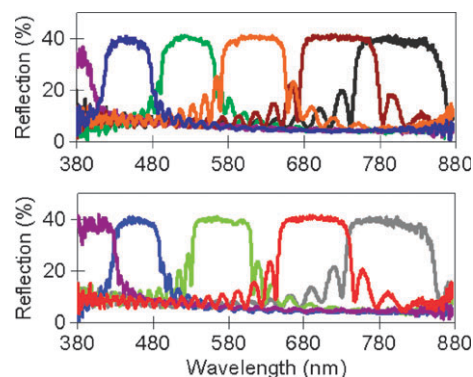


Fig. 5 Reflective spectra of 6.5 wt% chiral switch **4** in LC host E7 in a 5 μm thick planar cell at room temperature. Top: under UV light at 365 nm wavelength (5.0 mW cm^{-2}) with different times: 3 s, 8 s, 16 s, 25 s, 40 s and 47 s (from left to right). Bottom: under visible light at 520 nm wavelength (1.5 mW cm^{-2}) with different times: 2 s, 5 s, 9 s, 12 s and 20 s (from right to left).

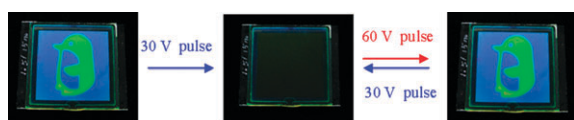


Fig. 6 Images of 5 μm thick homeotropic alignment cell with 4 wt% chiral switch **4** in LC host E7. The image was recorded in a planar state through a photomask by a UV light (left). The image was hidden by a low voltage pulse in a focal conic state (middle), and was made to reappear by a high voltage pulse (right). The image and background color in the cell can be adjusted by light.

change upon photoisomerization and result in the observed higher photoinduced change in the HTP and a better *cis* to *trans* conversion ratio upon visible light irradiation. When used as a dopant in the LC system, this results in a significant difference in the dose-rate change in reflection wavelength for a given concentration of dopant. This would allow for lower dopant concentrations to be used, lower phototuning intensities to maintain photostationary states, and faster overall tuning response from the systems employing the new compound.

Furthermore, like conventional cholesteric LCs, the chiral switch doped in LC media is able to be electrically switched to bistable display by using polymer stabilized or surface stabilized chiral nematic texture. It was recently discovered that one could take advantage of the bistability to create an optically addressed display whereby the image could be retained indefinitely and then erased electrically when desired.¹⁴ Even though the optically switched azo compounds are not thermally stable, an image can be made thermally stable and be retained indefinitely by electrically switching either the image or the image background to the focal conic state before it thermally relaxes. The image or its background is electrically selected by shifts in the electro-optic response curve due to a change in the HTP of the photosensitive chiral compound. An advantage of this display is that a thermally stable high resolution image can be captured without patterned electrodes or costly electronic drive and control circuitry, and retained indefinitely until electrically erased. Here such a light-driven device was made using the chiral switch **4**. The phototunable cholesteric layer sandwiched between two simple unpatterned transparent electrodes is sufficient. For example, an optical writing took place within seconds in a planar state through a photomask by a UV light. The reflective image can be hidden in focal conic texture by applying a 30 V pulse and be made to reappear by applying a 60 V pulse (Fig. 6). Moreover, by applying a 38 V pulse to this image so as to make the UV irradiated region go to the focal conic texture and the UV un-irradiated region go to the planar texture, the optically written image can be stored indefinitely since the planar and focal conic textures are stable.^{5,14}

In conclusion, 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 the entire visible region. 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.

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Notes and references

- S. Kawata and Y. Kawata, *Chem. Rev.*, 2000, **100**, 1777–1788; V. Balzani, M. Venturi and A. Credi, *Molecular Devices and Machines: A Journey into the Nanoworld*, Wiley-VCH, Weinheim, 2004; *Molecular Switches*, ed. B. L. Feringa, Wiley-VCH, Weinheim, 2001; N. P. M. Huck, W. F. Jager, B. de Longe and B. L. Feringa, *Science*, 1996, **273**, 1686–1688; A. Credi, *Aust. J. Chem.*, 2006, **59**, 157–169; W. R. Browne and B. L. Feringa, *Nat. Nanotechnol.*, 2006, **1**, 25–35; J. V. Hernandez, E. R. Kay and D. A. Leigh, *Science*, 2004, **306**, 1532–1537; D. Pijper, M. G. M. Jongejan, A. Meetsma and B. L. Feringa, *J. Am. Chem. Soc.*, 2008, **130**, 4541–4552.
- A. S. Kumar, T. Ye, T. Takami, B.-C. Yu, A. K. Flatt, J. M. Tour and P. S. Weiss, *Nano Lett.*, 2008, **8**, 1644–1648; R. A. Bissell, E. Cordova, A. E. Kaifer and J. F. Stoddart, *Nature*, 1994, **369**, 133–136; S. T. Fletcher, F. Dumur, M. M. Pollard and B. L. Feringa, *Science*, 2005, **310**, 80–82; V. Balzani, A. Credi, F. M. Raymo and J. F. Stoddart, *Angew. Chem., Int. Ed.*, 2000, **39**, 3348–3391.
- Photochromism: Memories and Switches, ed. M. Irie, Special Issue *Chem. Rev.*, 2000, **100**, 1683–1890; R. Eelkema and B. L. Feringa, *Org. Biomol. Chem.*, 2006, **4**, 3729–3745; T. Ikeda, *J. Mater. Chem.*, 2003, **13**, 2037–2057; S. Pieraccini, S. Masiero, G. P. Spada and G. Gottarelli, *Chem. Commun.*, 2003, 598–599; A. Urbas, V. Tondiglia, L. Natarajan, R. Sutherland, H. Yu, J.-H. Li and T. Bunning, *J. Am. Chem. Soc.*, 2004, **126**, 13580–13581; Q. Li, L. Li, J. Kim, H.-P. Park and J. Williams, *Chem. Mater.*, 2005, **17**, 6018–6021; R. Eelkema, M. M. Pollard, J. Vicario, N. Katsonis, B. S. Ramon, C. W. M. Bastiaansen, D. J. Broer and B. L. Feringa, *Nature*, 2006, **440**, 163.
- S. Pieraccini, G. Gottarelli, R. Labruto, S. Masiero, O. Pandolini and G. P. Spada, *Chem. Eur. J.*, 2004, **10**, 5632–5639.
- E. Montbach, N. Venkataraman, A. Khan, I. Shiyonovskaya, T. Schneider, J. W. Doane, L. Green and Q. Li, *SID Digest Tech. Pap.*, 2008, 919–922; N. Venkataraman, G. Magyar, E. Montbach, A. Khan, T. Schneider, J. W. Doane, L. Green and Q. Li, *Proc. Int. Display Res. Conf.*, 2008, **28**, 101–103.
- Q. Li, L. Green, N. Venkataraman, I. Shiyonovskaya, A. Khan, A. Urbas and J. W. Doane, *J. Am. Chem. Soc.*, 2007, **129**, 12908–12909; T. J. White, R. L. Bricker, L. V. Natarajan, N. V. Tabiryan, L. Green, Q. Li and T. J. Bunning, *Adv. Funct. Mater.*, 2009, **19**, 3484–3488.
- R. Eelkema, M. M. Pollard, N. Katsonis, J. Vicario, D. Broer and B. L. Feringa, *J. Am. Chem. Soc.*, 2006, **128**, 14397–14407; N. Tamaoki, *Adv. Mater.*, 2001, **13**, 1135–1147; T. Yoshioka, T. Ogata, T. Nonaka, M. Moritsugu, S. N. Kim and S. Kurihara, *Adv. Mater.*, 2005, **17**, 1226–1229; Y. Yu, M. Nakano and T. Ikeda, *Nature*, 2003, **425**, 145; V. A. Mallia and N. Tamaoki, *Chem. Soc. Rev.*, 2004, **33**, 76–84.
- R. A. van Delden, N. Koumura, N. Harada and B. L. Feringa, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 4945–4949.
- R. Eelkema and B. L. Feringa, *Chem.-Asian J.*, 2006, **1**, 367–369.
- M. Mathews and N. Tamaoki, *J. Am. Chem. Soc.*, 2008, **130**, 11409–11416.
- L. Green, Y. Li, T. White, A. Urbas, T. Bunning and Q. Li, *Org. Biomol. Chem.*, 2009, **7**, 3930–3933.
- I. Dierking, *Textures of Liquid Crystals*, Wiley-VCH, Weinheim, 2003.
- J. Chen, S. M. Morris, T. D. Wilkinson and H. J. Coles, *Appl. Phys. Lett.*, 2007, **91**, 121118.
- Q. Li, L. Green, J. W. Doane, A. Khan, N. Venkataraman and I. Shiyonovskaya, *US Patent Application Publication*, 2007, 02307906.