ChemPubSoc Europe

DOI: 10.1002/chem.201403705

CHEMISTRY
A European Journal
Full Paper

Molecular Switches

Rationally Designed Axially Chiral Diarylethene Switches with High Helical Twisting Power

Yannian Li,[a] Mengfei Wang,[a] Hao Wang,[a] Augustine Urbas,[b] and Quan Li*[a]

Abstract: Three rationally designed axially chiral diarylethene switches were synthesized and their application as chiral dopants for phototunable cholesteric liquid crystal devices was investigated. Design of these molecules was based on the combination of photochromic dithienylcyclopentene core with bridged binaphthyl units as chiral precursors. Aromatic groups were introduced to the molecules at 6,6′-positions of binaphthyls through a Suzuki–Miyaura coupling reaction. Their helical twisting powers (HTPs) are significantly higher than those of the known chiral diarylethenes reported as chiral dopants so far. Photocyclization of these molecules upon light irradiation brought out dramatic variation in HTPs between different states. The primary colors, red, green, and blue, were obtained in reflection on light irradiation and with thermal stability. Moreover, a multi-switchable photodisplay was demonstrated using one of these chiral molecular switches.

Introduction

Photochromic molecules that can reversibly transform between different forms upon light irradiation have proven extremely fascinating for the design and creation of intelligent functional materials and devices.[1] Among various kinds of photochromic molecules, diarylethenes are of particular interest owing to their superior thermal stability and excellent fatigue resistance, which is crucial for their applications.[2] Upon irradiation with UV light, diarylethenes can transform from the colorless ring-open form to the colored ring-closed form, whereas the reverse isomerization occurs only with visible light irradiation and the ring-closed forms are thermally stable. Because of the different physical and chemical properties at different states, the reversible switching constitutes the basis for the applications of diarylethenes in various areas, such as memories and switches.

In recent years, chiral diarylethenes have found important application in phototunable liquid crystal (LC) materials, especially as chiral dopant for the fabrication of photoresponsive cholesteric LCs (CLCs).[3] CLCs can be formulated by doping a chiral molecule into an achiral nematic LC and the resulting mixture can self-organize into a helical superstructure, that is, cholesteric phase, which can selectively reflect light according to Bragg's law.[4] The ability of a chiral dopant to twist a nematic phase is quantified as helical twisting power (HTP, β) and expressed as $\beta = 1/(PC)$, where P is the pitch length of the helical structure and C is the molar fraction of the chiral dopant. The reflection wavelength of CLCs is defined as $\lambda = nP$, where n is the mean refractive index of the LC medium. When chiral diarylethenes are employed as chiral dopants, the molecular conformation change during photoisomerization will bring out variation in HTPs accompanied by tuning in pitch length and reflection wavelength (Figure 1), which would open the door for CLCs to applications such as in color filters and reflectors,[5] tunable lasers,[6] and optically addressed displays[7] that require no driving electronics and can be made flexible.

Undoubtedly, high HTP is the most desirable attribute of a chiral dopant for device performance. Low HTPs will give rise to the requirement of high doping concentrations, which often

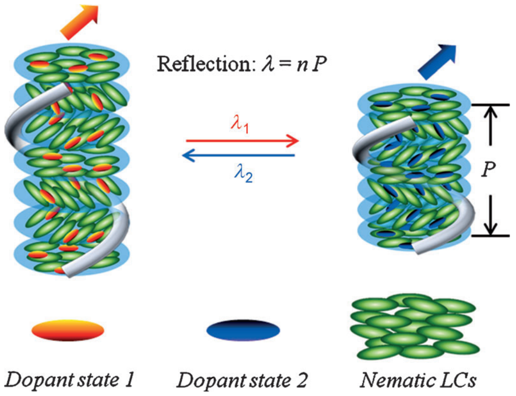

Figure 1. Illustration of the reversible tuning of the reflection wavelength in cholesteric liquid crystals doped with chiral photochromic molecules.

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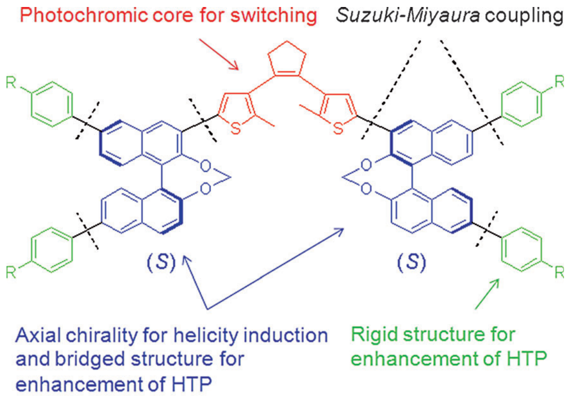
[a] Dr. Y. Li,+ M. Wang,+ H. Wang, Prof. Q. Li
Liquid Crystal Institute and Chemical Physics Interdisciplinary Program
Kent State University, Kent, OH, 44240 (USA)
Fax: (+1) 330-672-2796
E-mail: qli1@kent.edu

[b] Dr. A. Urbas
Materials and Manufacturing Directorate
Air Force Research Laboratory WPAFB, OH, 45433 (USA)

[+] These authors contributed equally to this work.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201403705.

leads to phase separation and/or coloration, and alters the desired physical properties of LC host. As an example of pursuing high HTPs, an azobenzene dopant has been reported with HTP up to 304 μm^{-1}.[8] For the diarylethenes dopants, it turns out that the HTPs have been dramatically increased in our recent reports;[3j–m] however, there are still considerable room to improve. In continuation with our previous work on light-driven chiral molecular switches, here we report three new chiral diarylethene molecules with very high HTPs (Figure 2). The intent behind the design of these molecules is based on following criteria: 1) a widely used dithienylcyclopentene core was selected for photoswitching purpose; 2) binaphthyl derivatives, especially bridged ones, have been proven to be powerful helicity inducers and therefore they were linked to photochromic core by Suzuki–Miyaura coupling;[9] and 3) rigid structures normally enhance the HTPs and additional aromatic rings were introduced through the 6 and 6′ positions of binaphthyl moiety with another Suzuki–Miyaura coupling reaction. This type of structure may resemble the rod-like LC molecules, and their dopant-host compatibility may also result in high HTPs.[10]

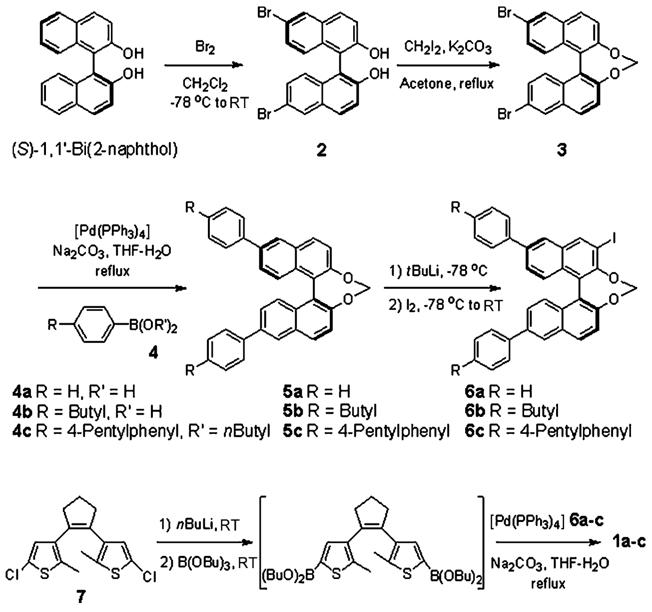


1a : R = H; **1b** : R = Butyl; **1c** : R = 4-Pentylphenyl

Figure 2. Design and chemical structures of axially chiral dithienylcyclopentene molecules **1a–c**.

Results and Discussion

The synthesis of the three compounds is depicted in Scheme 1. Intermediates **6a–c** were prepared starting from (*S*)-1,1′-bi(2-naphthol), which was brominated followed by reaction with diiodomethane to give the bromo-substituted bridged binapthyl derivative **3** in excellent yield. The Suzuki–Miyaura reaction of **3** with corresponding boronic acid or ester in the presence of palladium catalyst and sodium carbonate afforded coupling product **5a–c**, which was treated with *tert*-butyllithium at −78 °C followed by quenching with iodine. By controlling the ratio of *tert*-butyllithium to **5a–c**, mono-iodide product **6a–c** was achieved in acceptable yield. Dichloride **7** is a well-known intermediate for dithienylcyclopentene synthesis and was prepared according to a known method.[11] By conversion of **7** to bis(boronic ester) and another Suzuki–Miyaura coupling with **6a–c**, compounds **1a–c** were successfully synthesized in good yields.



Scheme 1. Synthesis of **1a–c**.

All three of the compounds are thermally and chemically stable, and their photoresponsive properties were initially characterized in organic solvent. For example, the UV/Vis spectra of **1a** in hexane exhibited absorption in UV region, and there was no absorption observed in the visible region (Figure 3). Upon UV irradiation, the solution color changed immediately from

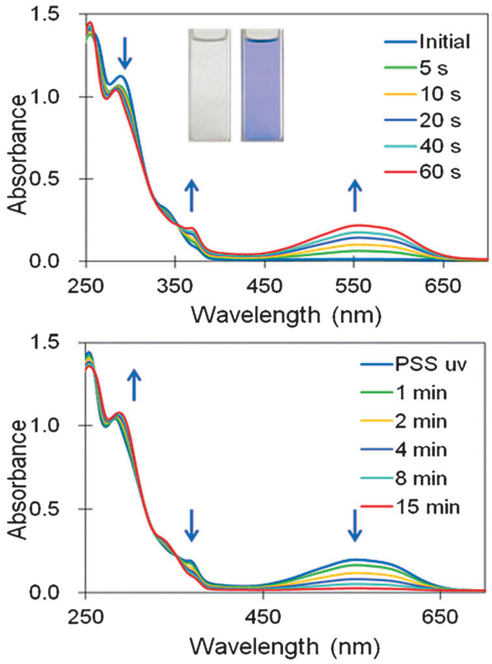


Figure 3. Absorption spectra changes of **1a** in hexane (10 μM) upon UV irradiation at 310 nm (30 mW cm^{-2}, top), followed by visible irradiation at 550 nm (30 mW cm^{-2}, bottom). Inset: solution color change from colorless to purple upon UV irradiation.

colorless to purple (Figure 3, inset). Accordingly, there was a gradual decrease observed in the absorption band in UV region accompanied by the appearance of a new absorption band in the visible region with a maximum at 558 nm. This is the characteristics of photochromic behavior, indicating that the transformation of **1 a** from its open form to the closed form.[2] The photostationary state (PSS$_{UV}$) was achieved within 60 s and this irradiated state was thermally stable as monitored by absorption spectra (Supporting Information, Figure S3). The reverse isomerization to open forms was realized by visible light irradiation at 550 nm in 15 min and the absorption spectra restored to initial state. The fatigue resistance of the photoisomerization process was examined by repeated and alternative irradiation with UV and visible light over many cycles (Supporting Information, Figure S3). No obvious degradation was observed.

The chiroptical properties of these compounds were investigated by CD spectroscopy at room temperature. As shown in Figure 4, The CD spectra of **1 a** exhibited strong bisignated exciton couplet between 230 and 280 nm (Figure 4), which is related to the coupling of the two ^1B_b transitions located on distinct naphthalene rings.[12] The intensive positive exciton couplet at 267 nm associated with negative couplet at 248 nm reflects the absolute *S* configuration of the binaphthyl moiety in the molecule. The couplets at around 300 and 340 nm are attributed to the ^1L_a and ^1L_b transitions of naphthalene. It is noteworthy here that these couplets appeared at longer wavelength than where they typically locate. For example, the ^1B_b couplets for binaphthyls were normally found between 200–250 nm for binapthyl derivatives compared with 230–280 nm observed in these compounds. This might result from the extended conjugation systems with the incorporation of aromatic groups into binapthyl units. Upon irradiation at 310 nm, the ^1B_b exciton couplets showed a slight bathochromic shift associated with variance in intensity. Distinct changes were also observed for ^1L_a and ^1L_b couplets. These changes of CD spectra are actually a sign of the conformation change in binaphthyl moiety with variation in dihedral angle.[13] Although the binaphthyls in these three compounds are fixed with a tether and thus have less flexibility, a slight variation of the dihedral angle is still possible, which may cause dramatic changes in chiroptical properties.[3j–m]

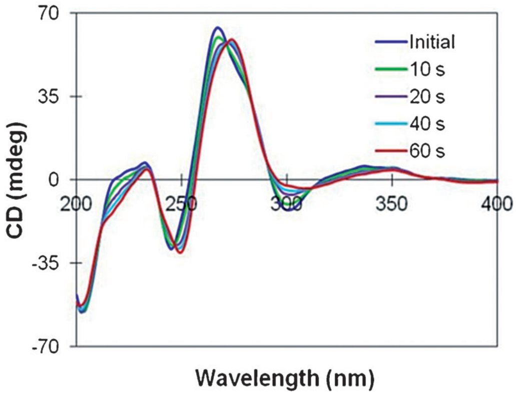


Figure 4. CD spectra changes of **1 a** in hexane (10 μM) upon UV irradiation at 310 nm.

It is known that the photocyclization of diarylethene molecules generates a pair of enantiomers with *S,S* or *R,R* configuration of two newly generated chiral centers derived from antiparallel style of open form. In the presence of axial chirality of the binaphthyl units, the closed form existed as two diastereomers with chiralities of (*S,S,S,S*) and (*S,R,R,S*) (Supporting Information, Figure S5). However, no Cotton effects in CD spectra were observed in the visible region corresponding to the absorption band of the closed forms of all three compounds, indicating that no diastereoselective photoisomerization occurred in photoisomerization process. Therefore the chiroptical properties of **1 a**–**c** and the related changes upon UV irradiation are mainly attributed to the conformation change of binaphthyl units and the variation in dihedral angle.

Inspired by the photoisomeization in organic solvent and chiroptical properties change, we examined their photoresponsive behavior in liquid crystals medium as chiral dopants. At first, compound **1 a** was doped into commercially available nematic LC 4-pentyl-4′-cyanobiphenyl (5CB). Surprisingly, it was found cholesteric phases were induced even at very low doping concentration of 0.1 mol % as confirmed by the observation of characteristic fingerprint and oily streak textures (Figure 5).[14] This indicated that **1 a** exhibited very high HTP at the initial state. When a mixture of 0.26 mol % of **1 a** in 5CB was filled into a wedge cell, the photoinduced pitch change was directly evidenced by the shortening in the distance between two adjacent Cano's lines upon UV irradiation (Figure 6). The pitch length and the HTPs were measured using the well-known Cano's method;[15] that is, the pitch length $P = 2R\tan\theta$, where the R is the distance between two adjacent Cano's line and θ is the wedge angle of the cell. By doping different concentrations of **1 a**, the inverse of the pitch ($1/P$) proportionally increases with increase in the doping concentration and the absolute values of HTP are then determined as the slopes by plotting $1/P$ against dopant concentration. The HTPs of **1 a** at the initial state was calculated to be 205 μm^{-1}, which was increased to 266 μm^{-1} upon UV irradiation.

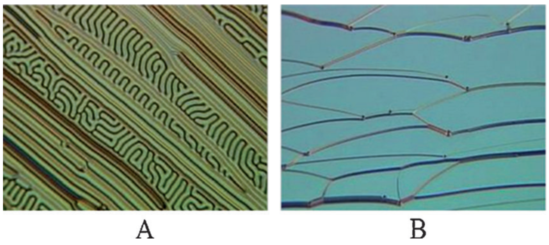


Figure 5. Fingerprint texture (A) and oily streak texture (B) of 0.1 mol % **1 a** in LC 5CB observed in a homeotropic cell and homogeneous cell, respectively.

By using similar method, the HTPs of all of these compounds at different states were determined and are summarized in

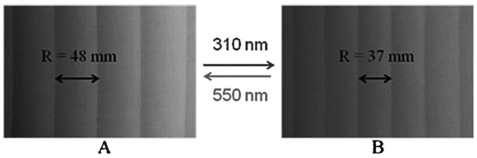


Figure 6. The Cano's lines and their distance change of 0.26 mol% of **1 a** in LC 5CB before (A) and after (B) UV irradiation with 310 nm.

Table 1. HTPs of **1 a–c** at different states in nematic LC hosts.

Dopant	LC host[a]	HTP β_M [μm^{-1}] Initial	PSS$_{310nm}$	PSS$_{550nm}$	$\Delta\beta_M/\beta_M$[b]
1 a	5CB	+205	+266	+208	+30
1 a	E7	+149	+172	+150	+15
1 a	Zli-1132	+188	+244	+191	+29
1 b	5CB	+248	+239	+246	−4
1 b	E7	+173	+156	+172	−10
1 b	Zli-1132	+224	+219	+222	−2
1 c	5CB	+278	+223	+275	−20
1 c	E7	+224	+190	+220	−15
1 c	Zli-1132	+256	+234	+254	−9

[a] E7 is a eutectic mixture of LC components commercially designed for display applications, and 5CB is 4′-pentyl-4-biphenylcarbonitrile. Zli-1132 is a mixture of 4-(4-alkylcyclohexyl)benzonitrile and 4-(4-alkylcyclohexyl)-4′-cyanobiphenyl derivatives. [b] Percent change in βM observed between initial state and PSS310nm.

Table 1. Their handedness were also determined by contact method and the sign "+" represents a right-handed cholesteric phase.[16] All three of the compounds induced right-handed CLCs in different LC hosts. It was found that they exhibit very high HTPs at both states. These values are much higher than those in our previous reports on high HTP diarylethene dopants with a value of 156 μm^{-1}.[3j] The HTP of **1 c** in 5CB is as high as 278 μm^{-1}, which is the highest value among all reported chiral diarylethene dopants to date. It is interesting that the three compounds exhibit different photoresponsive behavior as chiral dopants. All the HTPs of **1 a** in three LC hosts increased dramatically upon UV irradiation. **1 b** had a slightly higher HTP than **1 a** at the initial state, which experienced a minor decrease during photoisomerization. **1 c** showed the highest HTPs among three compounds at open forms; however, a relatively larger decrease was observed during the transformation into closed forms. Using different LC hosts for the same dopant resulted in different intermolecular associations between the dopant and the host, as revealed by the different HTP values and the change magnitude of HTP. 5CB gave the highest HTPs for all three compounds with largest change for **1 a** and **1 c**, while E7 resulted in relatively lower HTPs than other two hosts.

It is established that the dihedral angle in binaphthyl derivative plays key roles in their cholesteric induction behaviors, such as HTP and handedness of induced cholesteric phase.[9b] Both the *transoid* conformation ($\theta > 90^\circ$) and the *cisoid* conformation ($\theta < 90^\circ$) of binaphthyl derivatives can efficiently induce CLCs with high HTPs, while the *quasi-orthogonal* conformations ($\theta \sim 90^\circ$) only have very weak induction ability. For *S* configuration, the *transoid* conformation induces a right-handed CLC and the *cisoid* conformation results in a left-handed CLC. The minor variation in θ may cause a dramatic difference in the cholesteric induction abilities, that is, HTPs. All three compounds induced right-handed cholesteric phase which resulted from the *cisoid* form of bridged binaphthyl units. The very high HTPs of these three compounds may originate from our molecule design as aforementioned. The methylene bridged binaphthyls are stabilized as *cisoid* conformations and have very powerful helicity induction. The incorporation of aromatic groups at the 6 and 6′ position and the resulting elongated structures are more compatible with rod-like nematic mesogens with high HTPs. The variation in HTPs upon light irradiation might be a result of a molecular conformation change and the subtle dopant–host interactions.

On the basis of the high HTPs of **1 a** and the dramatic increase in LC 5CB, we determined to tune the reflection wavelength in the visible region. A mixture of 1.3 mol% of **1 a** in 5CB was capillary-filled into a 5 μm thick glass cell with antiparallel rubbing directions. The cell was painted black on one side and the reflection spectra were recorded. As seen in Figure 7, the reflection color of the cell at the initial state was red with a central reflection wavelength of ca. 610 nm. Upon UV irradiation for 20 s, the reflection wavelength shifted to ca. 550 nm and the cell showed a green reflection color, which was further tuned to blue with a reflection wavelength of ca. 480 nm at PSS$_{310nm}$. The reverse process was achieved with 550 nm visible-light irradiation and it took about 10 min for the LC mixture to restore the initial state. It is worth noting that the LC mixture exhibited superior thermal stability at any

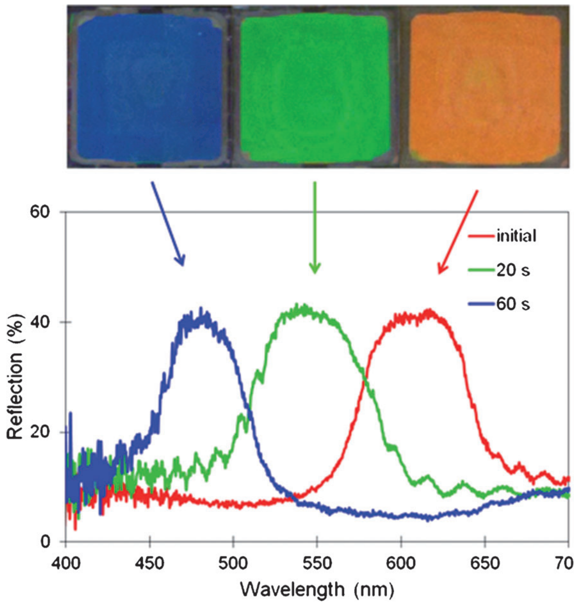


Figure 7. Reflection color changes observed in cell (2 cm×2 cm) and corresponding reflection spectra of 1.3 mol% of **1 a** in 5CB upon UV irradiation at 310 nm for 0 s (red), 20 s (green), and 60 s (blue).

irradiated state, which was revealed by no obvious reflection wavelength shifting when the cell was stored in the dark. The excellent fatigue resistance was examined by the repeated switching between the initial state and PSS_{310nm} over many cycles with no degradation in cell properties detected. Combined with the superior thermal stability and excellent fatigue resistance, the reflection color tuning enabled by **1a** is extremely promising for future applications.

The photo-addressed display utilizing **1a** as chiral dopant was also demonstrated in Figure 8. The same cell in Figure 7 was used and the central square area was coated with ITO layer. The reflection color of the cell was driven to blue with UV irradiation. After covering with a photomask, the symbol "β" with green reflection was recorded by visible light irradiation at 550 nm (Figure 8A). The image recorded was thermally stable and can be erased by UV irradiation. The cell was rewritable many times, which is ascribed to the excellent fatigue resistance of the chiral dopant **1a**. More interestingly, when a voltage of 20 V was applied across the cell, the LC mixture in ITO coated area was switched from planar state to focal conic state, which is a scattering, multidomain structure with random alignment of the cholesteric helices. The scattered light buried the image, as shown in Figure 8B. The image can be stored at this state and reappear by simply applying a mechanical force onto the cell (Figure 8C). The LC mixture returned to planar state owing to the shear-flow-induced alignment effect.[8h]

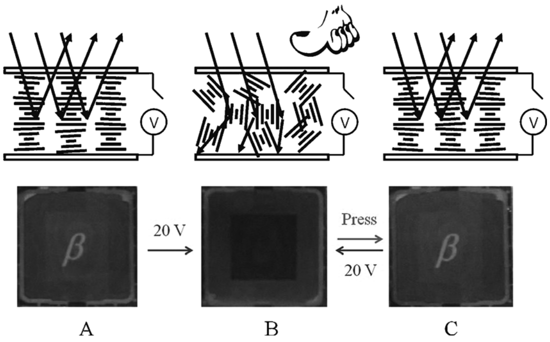


Figure 8. A photo-addressed and multi-switchable CLC display in a planar state through a photomask (A). The image was hidden by applying a voltage pulse in a focal conic state (B) and was made to reappear by a mechanical force (C). Note: the central square of the cell was coated with conductive ITO electrode layer. Top: representation of cholesteric textures; bottom: demonstration of an image.

Conclusions

We have rationally designed and synthesized three novel dithienylcyclopentene chiral dopants with high HTPs. The design of these compounds is based on the combination of photochromic core with binapthyl groups. Aromatic groups were introduced through the 6,6′-position of binaphtyl moiety. All of these compounds were found to exhibit exceptionally high HTPs and a HTP of 278 μm^{-1} was achieved, which is the highest value reported for chiral diarylethene dopant to date. Their photoresponsive behaviors were investigated and the reflection color tuning was demonstrated by using dopant **1a**. Furthermore, a thermally stable multi-switchable photodisplay was demonstrated. This work would provide new insight into designing and developing novel diarylethene molecules as photoresponsive liquid crystal materials for practical applications and further stimulate rational design of light-driven chiral switches or motors.

Experimental Section

Materials and methods

All of the chemicals and solvents were purchased from commercial supplies and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$. ^{1}H NMR (400 MHz) was recorded on a Bruker 400 spectrometer and ^{13}C NMR (50 MHz) was recorded on a Varian 200 spectrometer. Chemical shifts are in δ (ppm) with the residual solvent peak or TMS as the internal standard. The coupling constant J is reported in Hz. NMR splitting patterns are designated as follows: s singlet, d doublet, t triplet, m multiplet. Column chromatography was carried out on silica gel (230–400 mesh). Analytical thin-layer chromatography (TLC) was performed on commercially coated 60 mesh F_{254} glass plates. Spots were rendered visible by exposing the plate to UV light. Melting points are uncorrected. Elemental analysis was performed by Robertson Microlit Inc. Mass spectrum was taken by Mass Spectrometry and Proteomics Facility of Ohio State University. Textures and disclination line distance changes were observed by optical microscopy using a Leitz or Nikon polarizing microscope. UV/Vis spectra were measured by a PerkinElmer Lambda 25 Spectrometer. Circular dichroism (CD) spectra were recorded on a J-715 spectropolarimeter (Jasco Inc.) The UV and visible light irradiation was carried out with a xenon light source 100 W through a filter at 310 nm or 550 nm. Reflection spectra were examined with an Ocean Optics spectrometer collecting spectra in the dark. The achiral NLCs E7, 5CB, and Zli-1132 were used in the study. E7 is a eutectic mixture of LC components commercially designed for display applications, and 5CB is 4′-pentyl-4-biphenylcarbonitrile. Zli-1132 is a mixture of 4-(4-alkylcyclohexyl)-benzonitrile and 4-(4-alkylcyclohexyl)-4′-cyanobiphenyl derivatives.

Measurement of pitch and HTP

The CLCs were prepared by weighing appropriate amount of host liquid crystal and the dopant into a vial followed by mixing them with the addition of a few drops of dichloromethane. After evaporation of the solvent under reduced pressure, the mixture was loaded into the wedge cell by capillary action at room temperature. The pitch was then determined by measuring the intervals of Cano's lines appearing on the surfaces of wedge-type liquid crystalline cells. Three different concentrations were used by this method for each sample, and the HTP were determined by plotting $1/P$ (μm^{-1}) against concentration of the dopant C (mol %) according to the equation $\beta = 1/(PC)$.

Synthesis

Compound **3** was synthesized according to a previous report.[17] M.p.: 204–205 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 8.10$ (d, $J = 2.4$ Hz, 2H), 7.89 (d, $J = 8.8$ Hz, 2H), 7.50 (d, $J = 8.8$ Hz, 2H), 7.38 (dd, $J = 9.2$, 2.4 Hz, 2H), 7.31 (d, $J = 9.2$ Hz, 2H), 5.69 ppm (s, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 151.6$, 132.9, 130.5, 130.4, 129.6, 128.3, 125.9, 122.2, 119.2, 103.2 ppm. Elemental analysis calcd (%) for $C_{21}H_{12}Br_2O_2$: C 55.30, H 2.65; found: C 55.28, H 2.54. MS (MALDI): *m/z* 454 [*M*+H$^+$].

General procedure for the synthesis of 5a–c

The mixture of **3** (1 mmol), 4 (2.2 mmol), [Pd(PPh$_3$)$_4$] (0.1 mmol), aqueous Na_2CO_3 (20%, 5 mL), and THF (10 mL) was refluxed under nitrogen for 4 h. The reaction mixture was extracted with ethyl acetate (3×10 mL) and the combined organic layer was dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography to give the corresponding product **5a–c** in 85, 93, and 84% yields, respectively.

5a: M.p.: 265–266 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta=8.16$ (d, $J=2.0$ Hz, 2H), 8.06 (d, $J=8.8$ Hz, 2H), 7.75–7.72 (m, 4H), 7.65 (d, $J=8.8$ Hz, 2H), 7.61 (dd, $J=8.8$, 1.6 Hz, 2H), 7.54–7.47 (m, 6H), 7.40–7.38 (m, 2H), 5.73 ppm (s, 2H). ^{13}C NMR (CDCl$_3$, 50 MHz): $\delta=151.4$, 140.7, 137.7, 132.1, 131.3, 130.6, 128.9, 127.4, 127.3, 126.1, 126.0, 125.8, 121.4, 103.2 ppm. Elemental analysis calcd (%) for $C_{33}H_{22}O_2$: C 87.98, H 4.92; found: C 87.68, H 4.82. MS (ESI): *m/z* 473 [*M*+Na$^+$].

5b: M.p.: 175–176 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta=8.14$ (d, $J=1.6$ Hz, 2H), 8.04 (d, $J=9.2$ Hz, 2H), 7.66–7.59 (m, 8H), 7.51 (d, $J=8.4$ Hz, 2H), 7.30 (d, $J=8.4$ Hz, 4H), 5.73 (s, 2H), 2.68 (t, $J=8.0$ Hz, 4H), 1.70–1.63 (m, 4H), 1.46–1.37 (m, 4H), 0.96 ppm (t, $J=7.2$ Hz, 6H). ^{13}C NMR (CDCl$_3$, 50 MHz): $\delta=151.2$, 142.3, 138.0, 137.6, 132.1, 131.2, 130.5, 129.0, 127.4, 127.1, 126.0, 125.8, 121.3, 103.2, 35.3, 33.6, 22.4, 14.0 ppm. Elemental analysis calcd (%) for $C_{41}H_{38}O_2$: C 87.51, H 6.81; found: C 87.61, H 6.89. MS (ESI): *m/z* 585 [*M*+Na$^+$].

5c: M.p.: 276–278 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta=8.21$ (s, 2H), 8.07 (d, $J=8.8$ Hz, 2H), 7.81 (d, $J=8.4$ Hz, 4H), 7.72 (d, $J=8.4$ Hz, 4H), 7.68–7.67 (m, 4H), 7.59 (d, $J=8.4$ Hz, 4H), 7.54 (d, $J=8.8$ Hz, 2H), 7.29 (d, $J=8.4$ Hz, 4H), 5.75 (s, 2H), 2.67 (t, $J=8.0$ Hz, 4H), 1.72–1.65 (m, 4H), 1.39–1.36 (m, 8H), 0.93 ppm (t, $J=7.2$ Hz, 6H). ^{13}C NMR (CDCl$_3$, 50 MHz): $\delta=151.4$, 142.3, 140.2, 139.2, 137.9, 137.2, 132.2, 131.4, 130.6, 128.9, 127.6, 127.4, 126.9, 126.0, 125.7, 121.5, 103.2, 35.6, 31.6, 31.2, 22.6, 14.0 ppm. Elemental analysis calcd (%) for $C_{55}H_{50}O_2$: C 88.91, H 6.78; found: C 89.12, H 6.60. MS (ESI): *m/z* 742 [*M*+H$^+$].

General procedure for the synthesis of 6a–c

A *t*BuLi solution (1.2 mmol) was added to a solution of **5** (1 mmol) in anhydrous THF (10 mL) at −78 °C under nitrogen. The solution was stirred at this temperature for 1 h. A THF solution (5 mL) of iodine (1.3 mmol) was added to the reaction mixture. The reaction mixture was then allowed to warm to room temperature and stirred for an additional 10 h. The excess iodine was reduced with 1 M $Na_2S_2O_3$. The reaction mixture was poured into water and extracted with ethyl acetate (3×20 mL). The combined organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography to give the corresponding product **6a–c** in 52, 53, and 48% yields, respectively.

6a: M.p.: 228–230 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta=8.57$ (s, 1H), 0.97 (d, $J=0.8$ Hz, 1H), 8.07 (d, $J=8.4$ Hz, 1H), 8.03 (d, $J=1.2$ Hz, 1H), 7.74–7.69 (m, 4H), 7.62–7.59 (m, 4H), 7.54–7.47 (m, 5H), 7.41–7.39 (m, 2H), 5.74 (d, $J=3.2$ Hz, 1H), 5.70 ppm (d, $J=3.6$ Hz, 1H). ^{13}C NMR (CDCl$_3$, 50 MHz): $\delta=151.6$, 149.4, 140.5, 140.3, 139.5, 138.4, 137.8, 133.4, 132.1, 131.1, 131.0, 128.9, 127.6, 127.53, 127.46, 127.3, 126.7, 126.2, 126.1, 126.0, 125.7, 124.9, 121.3, 102.6, 90.7 ppm. Elemental analysis calcd (%) for $C_{33}H_{21}IO_2$: C 68.76, H 3.67; found: C 68.87, H 3.68. MS (ESI): *m/z* 599 [*M*+Na$^+$].

6b: M.p.: 106–108 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta=8.56$ (s, 1H), 8.14 (s, 1H), 8.05 (d, $J=8.8$ Hz, 1H), 8.02 (s, 1H), 7.66–7.58 (m, 8H), 7.52 (d, $J=8.8$ Hz, 1H), 7.31 (d, $J=8.4$ Hz, 4H), 5.75 (d, $J=3.6$ Hz, 1H), 5.70 (d, $J=3.6$ Hz, 1H), 2.69 (t, $J=8.0$ Hz, 4H), 1.71–1.63 (m, 4H), 1.46–1.37 (m, 4H), 0.97 ppm (t, $J=7.2$ Hz, 6H). ^{13}C NMR (CDCl$_3$, 50 MHz): $\delta=151.4$, 149.3, 142.6, 142.3, 139.4, 138.4, 137.84, 137.75, 137.6, 133.5, 132.1, 131.0, 130.9, 129.02, 128.98, 127.5, 127.2, 127.1, 126.7, 126.2, 126.0, 125.8, 125.7, 124.5, 121.2, 102.6, 90.6, 35.3, 33.6, 22.4, 14.0 ppm. Elemental analysis calcd (%) for $C_{41}H_{37}IO_2$: C 71.51, H 5.42; found: C 71.48, H 5.31. MS (MALDI): *m/z* 688 [*M*+H$^+$].

6c: M.p.: 128–130 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta=8.58$ (s, 1H), 8.21 (d, $J=1.2$ Hz, 1H), 8.09–8.07 (m, 2H), 7.81–7.78 (m, 4H), 7.71 (d, $J=7.6$ Hz, 4H), 7.69–7.58 (m, 8H), 7.54 (d, $J=8.8$ Hz, 1H), 7.29 (d, $J=8.0$ Hz, 4H), 5.76 (d, $J=3.6$ Hz, 1H), 5.71 (d, $J=3.2$ Hz, 1H), 2.67 (t, $J=7.6$ Hz, 4H), 1.70–1.66 (m, 4H), 1.39–1.36 (m, 8H), 0.93 ppm (t, $J=7.2$ Hz, 6H). ^{13}C NMR (CDCl$_3$, 50 MHz): $\delta=151.6$, 149.5, 142.4, 142.3, 140.5, 140.3, 139.5, 139.1, 138.8, 138.0, 137.9, 137.8, 137.4, 133.5, 132.1, 131.2, 128.9, 127.6, 127.5, 126.9, 126.7, 126.1, 125.8, 125.7, 124.7, 121.3, 102.7, 90.7, 35.6, 31.6, 31.2, 22.6, 14.0 ppm. Elemental analysis calcd (%) for $C_{55}H_{49}IO_2$: C 76.03, H 5.68; found: C 76.31, H 5.57. MS (MALDI): *m/z* 868 [*M*+H$^+$].

General procedure for the synthesis of 1a–c

A solution of *n*BuLi (1 mmol) was added dropwise to a solution of **7** (0.5 mmol) in anhydrous THF (10 mL), and the mixture was stirred at room temperature for 1 h. Then B(OBu)$_3$ (345 mg, 1.5 mmol) was added and stirred at room temperature for another 1 h followed by addition of **6** (1 mmol), 20% Na_2CO_3 (8 mL) aqueous solution, and [Pd(PPh$_3$)$_4$] (0.03 mmol). The reaction mixture was heated to reflux and stirred for 10 h. After the mixture was cooled to room temperature, the organic layer was separated and the water layer was extracted with ethyl acetate (2×10 mL). The combined organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography to give corresponding product **1a–c** in 67, 73, and 75% yields, respectively.

1a: M.p.: 235–237 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta=8.26$ (s, 2H), 8.13 (d, $J=10.8$ Hz, 4H), 8.00 (d, $J=8.8$ Hz, 2H), 7.75–7.69 (m, 8H), 7.66–7.60 (m, 4H), 7.54 (s, 4H), 7.51–7.33 (m, 16H), 5.63–5.60 (m, 4H), 2.95–2.91 (m, 4H), 2.18 (s, 6H), 2.18–2.12 ppm (m, 2H). ^{13}C NMR (CDCl$_3$, 50 MHz): $\delta=151.3$, 147.8, 140.7, 140.6, 138.1, 137.6, 136.4, 136.1, 134.9, 134.1, 132.04, 131.96, 131.4, 130.6, 130.3, 128.8, 128.0, 127.6, 127.4, 127.3, 127.2, 127.13, 127.10, 126.1, 126.0, 125.8, 125.6, 121.3, 102.5, 38.4, 23.1, 14.3 ppm. Elemental analysis calcd (%) for $C_{81}H_{56}O_4S_2$: C 84.05, H 4.88; found: C 83.78, H 4.76. MS (MALDI): *m/z* 1156 [*M*+H$^+$].

1b: M.p.: 208–210 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta=8.24$ (s, 2H), 8.12 (d, $J=10.4$ Hz, 4H), 7.98 (d, $J=8.8$ Hz, 2H), 7.67–7.61 (m, 12H), 7.54 (s, 4H), 7.44 (s, 2H), 7.41 (d, $J=8.8$ Hz, 2H), 7.30 (d, $J=7.6$ Hz, 4H), 7.27–7.25 (m, 4H), 5.62 (d, $J=3.6$ Hz, 2H), 5.59 (d, $J=3.2$ Hz, 2H), 2.95–2.92 (m, 4H), 2.71- 2.64 (m, 8H), 2.17 (s, 6H), 2.18–2.15 (m, 2H), 1.69–1.63 (m, 8H), 1.44–1.37 (m, 8H), 0.99–0.94 ppm (m, 12H). ^{13}C NMR (CDCl$_3$, 50 MHz): $\delta=151.2$, 147.6, 142.3, 138.1, 138.0, 137.9, 137.6, 136.4, 136.0, 134.9, 134.2, 132.1, 132.0, 131.3, 130.5, 130.2, 128.9, 127.9, 127.5, 127.1, 127.0, 126.1, 125.7, 125.6, 121.2, 102.5, 38.4, 35.3, 33.6, 23.1, 22.4, 14.3, 14.0 ppm. Elemental analysis calcd (%) for $C_{97}H_{88}O_4S_2$: C 84.31, H 6.42, S 4.64; found: C 84.05, H 6.31, S 4.40. MS (MALDI): *m/z* 1380 [*M*+H$^+$].

1c: M.p.: 200–202 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta=8.26$ (s, 2H), 8.18 (s, 2H), 8.14 (d, $J=1.2$ Hz, 2H), 8.00 (d, $J=8.8$ Hz, 2H), 7.79 (dd, $J=6.8$, 1.6 Hz, 4H), 7.75–7.69 (m, 8H), 7.64 (d, $J=8.4$ Hz, 8H), 7.60–7.54 (m, 12 H), 7.45 (s, 2 H), 7.42 (d, $J=8.8$ Hz, 2 H), 7.27 (t, $J=8.0$ Hz, 8 H), 5.64 (d, $J=3.6$ Hz, 2 H), 5.62 (d, $J=3.6$ Hz, 2 H), 3.00–2.89 (m, 4 H), 2.69–2.63 (m, 8 H), 2.21 (s, 6 H), 2.21–2.15 (m, 2 H), 1.70–1.65 (m, 8 H), 1.40–1.35 (m, 16 H), 0.94–0.90 ppm (m, 12 H). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta=151.3$, 147.7, 142.2, 140.1, 139.2, 139.0, 137.89, 137.85, 137.6, 137.1, 136.4, 136.2, 135.0, 134.1, 132.1, 132.0, 131.4, 130.7, 130.3, 128.9, 128.1, 127.5, 127.44, 127.37, 127.3, 127.15, 127.12, 126.8, 126.1, 125.9, 125.7, 125.5, 121.3, 102.5, 38.2, 35.6, 31.6, 31.2, 23.2, 22.6, 14.3, 14.0 ppm. Elemental analysis calcd (%) for $C_{125}H_{112}O_4S_2$: C 86.17, H 6.48, S 3.68; found: C 86.16, H 6.22, S 3.49. MS (MALDI): m/z 1741 $[M+H^+]$.

Acknowledgements

This work is supported by the Air Force Office of Scientific Research (AFOSR FA9559-09-0254 and FA9559-09-1–0193).

Keywords: axial chirality · liquid crystals · molecular switches · photochromism · reflection color

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Received: May 27, 2014
Revised: July 10, 2014

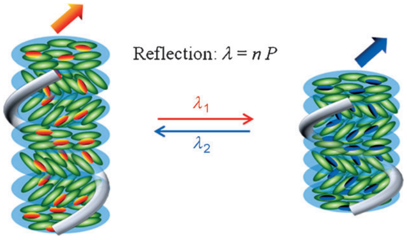
FULL PAPER

Molecular Switches

*Y. Li, M. Wang, H. Wang, A. Urbas, Q. Li**

■■ – ■■

Rationally Designed Axially Chiral Diarylethene Switches with High Helical Twisting Power



Three axially chiral diarylethene switches were synthesized and their photoresponsive properties were characterized in both organic solvent and liquid crystal media. These rigid dithienylcyclopentene structures exhibit very high helical twisting power. The primary colors, red, green, and blue, were obtained in reflection on light irradiation and with thermal stability, and a multi-switchable photodisplay was demonstrated.