A GENUINELY MULTIDISCIPLINARY JOURNAL

CHEMPLUSCHEM

CENTERING ON CHEMISTRY

# Accepted Article

**Title:** Binary Supramolecular Chirality "1/0" Switched by Hierarchical Photoisomerization of Flower-like Compound with a Binaphthol Core and Alkyl-Functionalized Azobenzene Side Chains

**Authors:** Hao Li, Jiaxin Hou, Jinglun Liao, Yancong Feng, Ben L. Feringa, Jiawen Chen, and Guofu Zhou



**To be cited as:** *ChemPlusChem* 10.1002/cplu.202000049

**Link to VoR:** http://dx.doi.org/10.1002/cplu.202000049

A Journal of ChemPubSoc Europe

WILEY-VCH www.chempluschem.org

WILEY-VCH

FULL PAPER

# Binary Supramolecular Chirality "1/0" Switched by Hierarchical Photoisomerization of Flower-like Compound with a Binaphthol Core and Alkyl-Functionalized Azobenzene Side Chains

Jiaxin Hou[a],[b], Jinglun Liao[a],[b], Yancong Feng[a],[b], Ben L. Feringa[a],[b], Jiawen Chen[a],[b]*, Hao Li[a],[b]*, and Guofu Zhou[a],[b]

[a] J. Hou, J. Liao, Prof. Y. Feng, Prof. B. L. Feringa, Prof. J. Chen, Prof. H. Li, and Prof. G. Zhou
Guangdong Provincial Key Laboratory of Optical Information Materials and Technology & Institute of Electronic Paper Displays,
South China Academy of Advanced Optoelectronics,
South China Normal University, Guangzhou 510006, China
E-mail: Lihao@m.scnu.edu.cn

[b] J. Hou, J. Liao, Prof. Y. Feng, Prof. B. L. Feringa, Prof. J. Chen, Prof. H. Li, and Prof. G. Zhou
National Center for International Research on Green Optoelectronics,
South China Normal University, Guangzhou 510006, China
E-mail: j.chen@m.scnu.edu.cn

**Abstract:** Chiral supramolecular assemblies are abundant in nature, and serve as inspiration for most of the man-made systems, but the control on chirality of artificial systems still remains a challenge. In this work, we developed a system where supramolecular chirality can be controlled between chirality and achirality, namely chiral "1/0" using a flower-like azobezene compound. Upon the photoisomerization by ultraviolet irradiation, terminal alkyl tails envelop the chiral "centre" with decreasing dihedral angle of the binaphthol moiety from 76.1° to 61.4°, like "closing petals". In the doped E7 matrix, this hierarchical conformational transition prevents from transferring charity to the host liquid crystal, resulting in a degradation from cholesteric phase (HTP value: 13.84 $\mu m^{-1}$) to achiral nematic phase.

## Introduction

In nature, chiral supramolecular assemblies are abundant in numerous creatures from microscopic units (e.g., DNA, protein, and biomembrane) to macroscopic structures (e.g., plant tissues, arthropod cuticle, and sea shells) and these chiral structures are bases of a lot of beautiful propeties. Therefore, chirality is crucial to structure, conformation, property, function. Supramolecular chirality of the whole system comes from interactions between chiral and achiral components, and the nonsymmetrical arrangement of achiral molecules via noncovalent intereations.1 It is very important to develop artificial chiral supramolecular systems for applications in areas of chemistry, biology, physics and materials.[2]

There are two key issues for supramolecular chirality: (1) transfer of chirality from molecular scale along all the length scales to macroscopical scale; (2) control of chirality for modulating macroscopic properties. In particular, the latter is viewed as an important challenge that is "still in its infancy" but "exciting in the future".[3] Due to complexity and flexibility of noncovalent interactions, it is difficult to change the self-assembly via direct conformational control of chiral units inside the supramolecular system. Some external factors such as solvent, temperature, sonication, photoirradiation, redox potential, and chemical additives, are needed to realizing the chirality control process. Light is usually regarded as one of the best options because of its high accurance, non-invasiveness and feasiblity.[1,4] In most cases, light-actived compound, such as azobenzene, is introduced into liquid crystal (LC) molecule[5-7], chiral dopant[8-13], polymer[14], and other systems, to obtain photo-controllability by its light-triggered conformational transformation. Other photochromic groups, e.g., diarylethenes[15], dithienylethenes[16,17], and oligobipyridyl ligands[18], are aslo embedded to dynamically self-assemble or disassemble into various helicates under light irradiation. In most of the cases, direct chiral reversal between R and S[9-11], cis- and trans-[5,7,8,11], or others[13,16,17], as well as amplification[14,19], are focused. Chiral on–off switching of the whole supramolecular system induced by light are with few examples.

In this work, we designed and synthesized a flower-like binaphthyl compound bearing azobenzene moities, and used it as a chiral dopant to switch the supramolecular chirality of the liquid crystal system. By ultraviolet light (UV) irradiation, the azobenzene units of the compound can induce dramatic trans–cis isomerization, as a result, the conformation of the compound changes. The side chains of the compound envelop chiral binaphthyl "centre", and the whole molecule appears like a flower "closing", and the interaction with the surrounding achiral LC hosts are therefore covered and the whole system shows no supramolecular chirality. Reversibly, visible light (Vis) can make it "blossoming", as opuntia flower behaves in day and night, and the chirality of the LC system is regained.

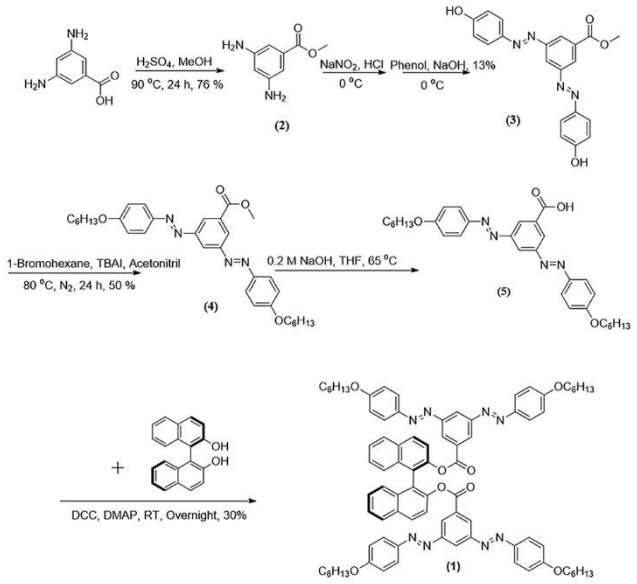
## Results and Discussion

In this work, we integrated chiral moiety and photosensitizer in one compound to form a flower-like photo-controllable switch. For the choice of chiral moiety, cholesterol[20] and binaphthyl[21] derivatives are two mostly used moieties. As reported previously, binaphthyl derivatives can induce large βm value up to hundreds $um^{-1}$ [22, 23], and behaved much better than cholesterol-modified azobenzenes[24]. In the molecular structures of these binaphthyl derivatives, steric hindrance may induce the carbon–carbon

10.1002/cplu.202000049




bridged bond between 1 and 1' position rotating to form different dihedral angles (θ) of the two naphthyl rings, and therefore induce some changes in helical structure and therefore affect the helical twisting power (HTP, evaluated by βm value).[25-27] As chromophore moiety, the selected azobenzene[28-30[ is more commonly used than fulgides[31], diarylethenes[32-34], spiropyrans[35[, and other photochromic moieties[36,37]. It can rapidly undergo trans–cis isomerization by ultraviolet (UV) exposure (~360 nm), to change the helical twisting power (HTP, evaluated by $\beta_m$ value) of the host LC system.[38-40] We introduced four photochromic azobenzene groups on both sides of the binaphthyl centre, to form a highly symmetric and flower-like dopant (i.e. compound 1 in **Scheme 1**) for the control of the supramolecular chirality of LC system.




**Scheme 1** Synthetic route of compound 1

**UV-Vis spectroscopic study**

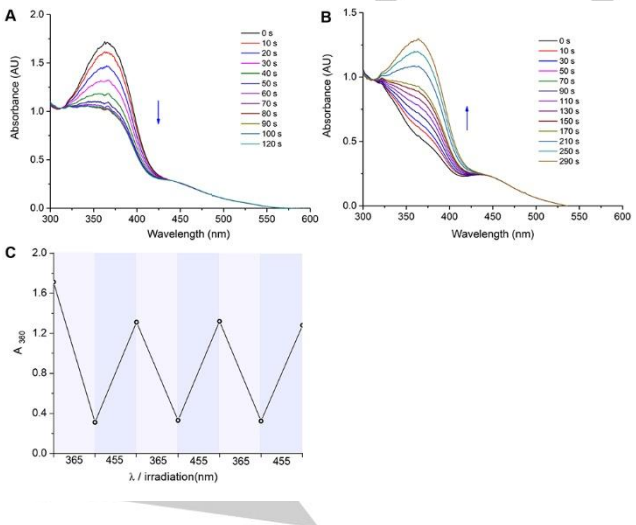



**Figure 1** UV-Vis spectra of the DMSO solution of compound 1 with the fixed concentration of $1.7\times10^{-5}$ mol·dm$^{-3}$ at 25 °C: irradiated by 365 nm light (A); irradiated by 455 nm light (B); absorbance-changing curve at 360 nm upon alternating irradiation of 365 and 455 nm light with duration of 3 minutes (C).

Photochemical properties of compound 1 were firstly characterized in dimethyl sulfoxide (DMSO) solution by UV-Vis spectroscopy. **Figure 1A** showed a strong absorption band with the maximum absorption wavelength ($\lambda_{max}$) of 360 nm. Upon UV irradiation, this band decreased in intensity and two new adjacent bands appeared simultaneously in the region around 325 and 450 nm. Subsequent irradiation with 455 nm weakened the newly formed bands in intensity again, and the original band reappeared (see **Figure 1B**), which is a characteristic behavior of the azobenzene compound. The variation in absorbance at 360 nm was repeated three times *via.* alternating irradiation of 365 and 455 nm light (see **Figure 1C**). The photochemical switching process can be reproduced several times without significant fatigure.

**$^1$H-NMR spectroscopic study**

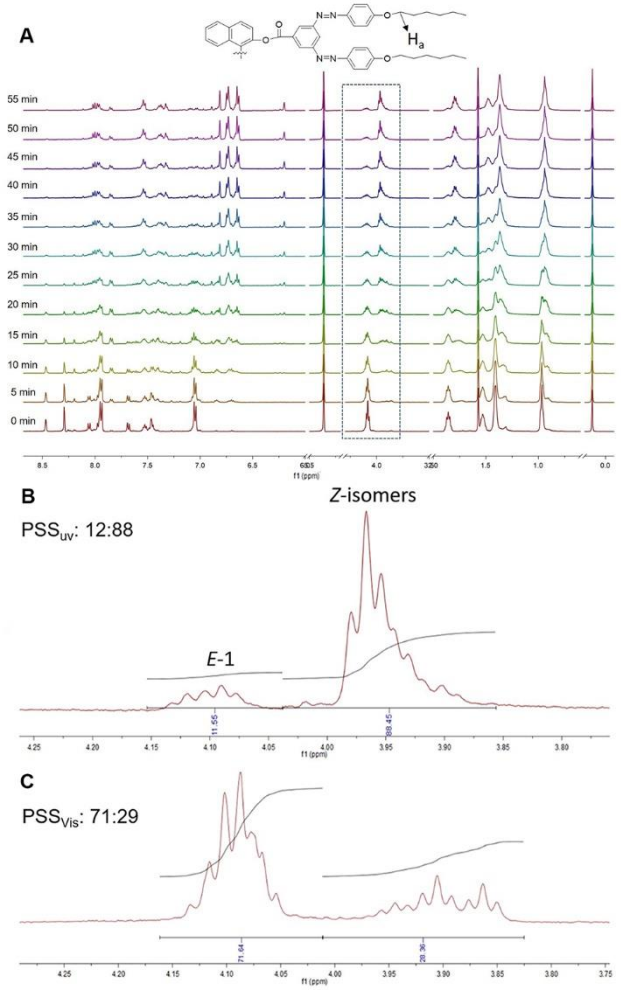



**Figure 2** Progressive formation and conversion of the compound 1 stereoisomers in the form of $^1$H-NMR spectral changes with increasing irradiation time at 365 nm.(A) (500 MHz; 298K; $CD_2Cl_2$) Enlarged views of partial 1H-NMR spectra (500 MHz; 298K; $CD_2Cl_2$): PSS mixture of *E*-1 after irradiated at 365 nm for 1.5 hours (B), and PSS mixture of *Z*-1 after irradiated at 455 nm for 1.5 hours (C).

The switching process of compound **1** was monitored by $^1$H-NMR spectrospcopy in $CD_2Cl_2$ as well (see **Figure 2A**). The spectra were recorded every 5 minutes upon UV light irradiation till no further change was observed. Starting from the solution containing only the trans-isomer (*E*-isomer) of compound 1, irradiation of 365 nm light resulted in appearance of new signals in both the aromatic and the aliphatic region. The NMR signals with the shift are corresponding to the protons adjacent to the azobenzene unit that undergo the photo-induced isomerization. There were some observed changes in the aliphatic region. In detail, the triplet at 4.10 ppm (i.e. $H_a$ in **Figure 2A**) shifted upfield to 3.95 ppm under UV irradiation (see **Figure 2B**). The integrals of the $H_a$ signal at 4.10 and 3.95 ppm indicates that the trans-cis (*E*→*Z*) photostationary state (PSS) is above 88%. Subsequent visible light (Vis) irradiation of the sample at PSS resulted in 60% reversion of the cis-(*Z*) stereoisomers to E azobenzene units (see **Figure 2C**). The incomplete Z→E switch may attribute to the above-mentioned fatigue of UV absorbance.

### Kinetic analyses

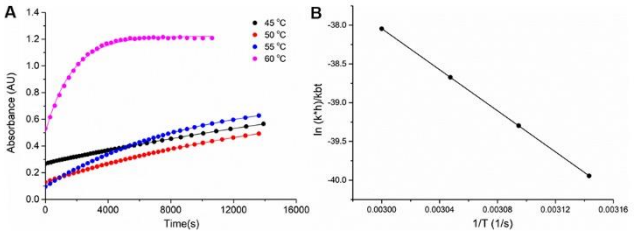



**Figure 3** 360 nm Absorbance-time curves of the DMSO solution of compound 1 with the fixed concentration of $1.7\times10^{-5}$ mol·dm$^{-3}$ at different temperatures (A), and related linear fitting according to Eyring kinetic equation (B).

**Figure 3A** shown UV-Vis absorbance-time variations during the heat-induced *Z*-to-*E* isomerization. By Eyring plot analysis, the activation parameters for thermal cis-trans (*Z*→*E*) inversion of compound **1** were obtained (see **Figure 3B**): the enthalpy of activation (ΔH) is 165.73 kJ mol$^{-1}$, and the entropy of activation (ΔS) is 187.08 J mol$^{-1}$ K$^{-1}$. According to Gibbs equation, the free energy of activation (ΔG) at 293.15 K is 110.89 kJ mol$^{-1}$ and correspond to a half-life of the thermal step at 293.15 K (i.e. 20 ℃) 1817.2 hours. It demonstrates that the Z isomers of compound **1** is very stable at room temperature.

### CD spectroscopic study

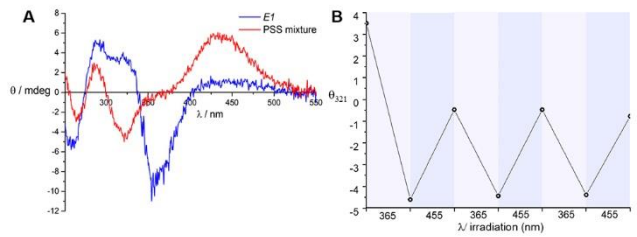



**Figure 4** Experimental CD spectra of E-1 and Z-1 isomers of compound 1 in DCM (A) and related CD signal-changing curve at 321 nm upon alternating irradiation of 365 and 455 nm light with every irradiation period of 3 minutes (B).

The switching process of compound **1** was investigated by CD spectroscopy as depicted in **Figure 4** as well. UV irradiation resulted in the disappearance of the CD signal around 360 nm, and the appearance of a new CD signal around 440 nm. This variation within the region from 250 to 550 nm indicates that, the photoisomerization of the side azobenzene moieties alters the dihedral angle of binaphthol centre. Vis irradiation can have a reverse effect on the conformation of compound **1**. When alternated irradiation applied, the CD signal can be regained, in accordance with the changing process of the $^1$H-NMR curve in **Figure 1C** (see **Figure 4B**). But the unavoidable molecular fatigue still hinders complete conformational recovery.

### Concentration dependence

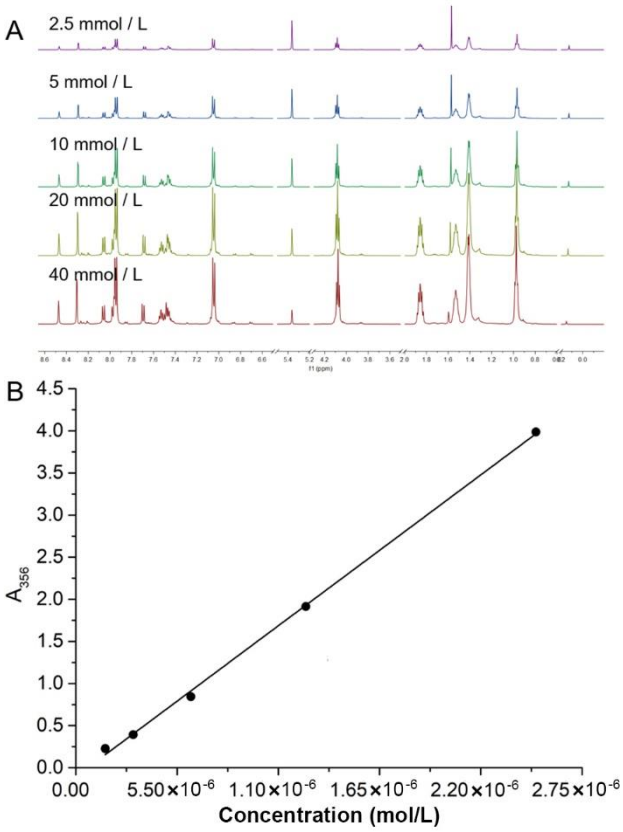



**Figure 5** $^1$H-NMR spectra (500 MHz, 298K, $CD_2Cl_2$; A) and UV absorbances of compound 1 with different concentration (356 nm, DCM; B).

Compound 1 was prepared as a series of solution ranging from 40 to 2.5 mmol•L$^{-1}$ and all the chemical shifts of $^1$H-NMR signals remain unchanged (see **Figure 5A**), indicating no self-aggregation. Similarly, UV absorbance at 356 nm shown with good linear relationship at lower concentration. Both results set a solid stage for the application in LC within a wide range of concentrations.

### HTP transition

In CLC system, compound 1 was used as photosensitive chiral dopant, to tune the helicity and the phase state of the host LC by the interaction with the host and the guest molecules. The HTP

(β) of compound 1 and its changes under photoirradiation were determined by the Grandjean–Cano method. By measurement, the initial value of HTP on weight percentage in cholesteric E7 is 13.84 $\mu m^{-1}$. Once UV light was irradiated for one hour, all the stripes completely disappeared (see **Figure 6A**). It indicates that the cholesteric phase of E7 change into nematic phase. In other words, the chirality of the whole CLC system disappears after UV irradiation. This change can be ascribed to the trans-cis (E→Z) isomerization of the azobenzene moieties. Reversibly, when Vis light was irradiated for one hour, these stripes reappeared and the measured HTP was 10.95 $\mu m^{-1}$. The recovered β value is lower than the initial one because of the PSS of the azobenzene. Just like the above mentioned, here is incomplete recovery originated from molecular fatigue.

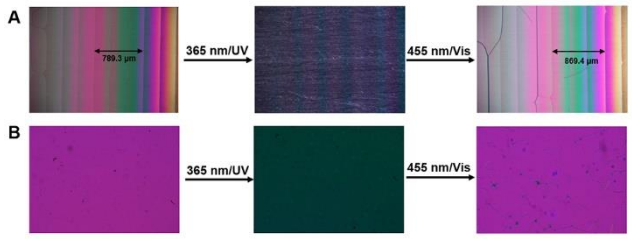



**Figure 6.** POM images of stripe-wedge Grandjean-Cano cell filled with 2 wt.% of compound **1** in E7 upon UV (365 nm) and Vis (455 nm) irradiation.(A) Reflection color POM images of 5 μm-thick planar cell filled with 2 wt.% of compound **1** in E7 upon UV (365 nm) and Vis (455 nm) irradiation.(B)

Furthermore, a mixture of 2 wt.% of compound **1** in E7 was capillary-filled into a 5 μm thick planar glass cell coated with a polyimide alignment layer. As shown in **Figure 6B**, the LC cell went from initial purple color to dark green color at PSS upon UV irradiation. UV light irradiation leads to the degradation of cholesteric E7 system, as well as a sharp decrease of LC reflection. The newly form state is thermally stable and can be further photochemically switched back with Vis irradiation. The regain of the color is the result of the reversed cis-trans (*Z*→*E*) isomerization upon Vis irradiation.

**Mechanism analyses**

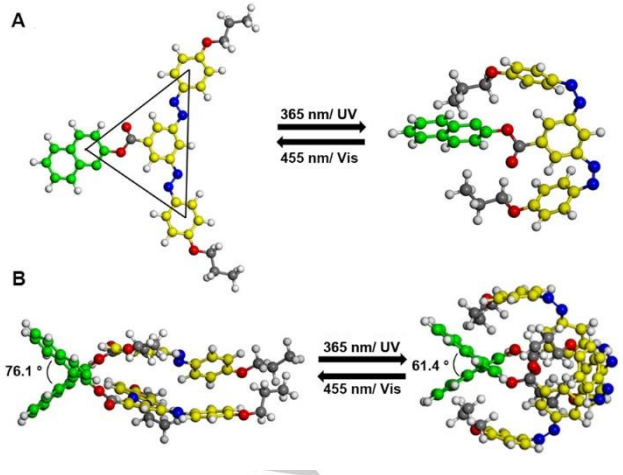
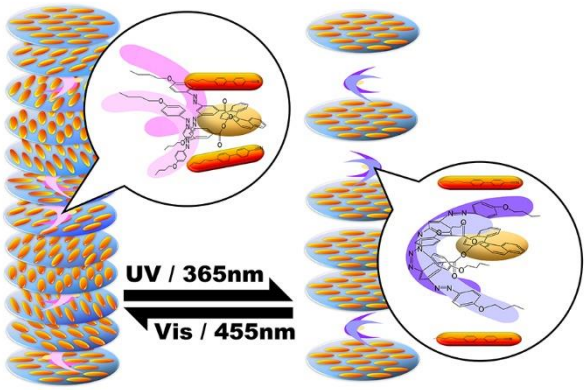



**Figure 7** Computational simulation of compound 1's conformations after 365 and 455 nm photoirradiation: half symmetrical molecule (A), whole symmetrical molecule (B) and its photo-switched 'blossoming-closing' mechanism.

In order to study the mechanism in more detail, we performed DFT calculation to simulate the conformational change of compound **1**. The naphthalene and two side azobenzene branches were entitled as three vertexes of triangle shape, repsepctively. The original symmetrical compound 1 acts like a blossoming "quatrefoil" with the "centre" dihedral angle of 76.1°. When UV light irradiates, the symertirc chiral dopant can isomerize from trans- to cis- conformation, and the benzene rings overturn and get close to the central naphthalene ring. At this conformation, the terminal alkyl chains seem to envelop this "centre" like "closing petals". At the same time, the dihedral angle between two naphthalene ring decreases to a smaller angle of 61.4°.




**Scheme 2** Chiral "1/0" photo-switching mechanism of compound 1 in E7.

Based on the above analyses, it can be found that, both the chromophore moiety and its alkyl tails are far away from the binaphthol "centre" before UV irradiation. Akagi et al. previously reported that, E7 with biphenyl moiety can interact with binaphthol by π–π interaction, suggesting to align parallelly to the axis of binaphthol.[41] These intermolecular interactions may enhance the compatibility between the guest chiral dopants and the host LC, and therefore induce chirality transferring to host LC for modulating HTP.[42-44] In our case, after UV irradiation, 4 azobenzene moieties isomerized from *E* to *Z*, pushing the chromophore moiety and the terminal alkyl tails to align crowdedly, so E7 molecules were extruded out of the enveloped binaphthol "centre". The weakened π–π interaction between E7 and chiral "centre" makes the host LC far from the guest dopant molecules. Thus, the chirality of dopant cannot be transferred to the host LC, and resulted in a dramatic decrease of HTP. As a result, the doped CLC system changes from CLC phase to nematic phase, along with increasing pitch to infinity and the HTP appears to be 0 (see **Scheme 2**).

We use a single-molecular photoswitch to control the supramolecular chirality and achirality of the LC system. The chromophoric switch we used can transit its own chirality to the host LC, and when irradiation is applied, it can drive the linked alkyl tails to envelop the chiral center so the chirality transferring to host LC is prevented. In other words, the conversion between

"blooming" and "closing" state is a reversible process and control the LC system from chiral and "achiral" .

## Conclusion

A symmetric photo-responsive chiral dopant, bearing axial binaphthol moiety as chiral center and azobenzene moieties as chromophore, was designed and synthesized in this work. Based on various characterizations, the chiral dopant shown reversible photoisomerization process and the Z-isomer is thermally stable at room temperature. In CLC system, a reversible change from cholesteric to nematic phase can be controlled when UV/Vis light was irradiated. The HTP and the pitch of CLC system can be controlled at the same time. Thus its optical property, e.g. reflectivity, can be reversiblly switched by photoirradiation.

According to computational simulation and molecular geometry optimization, photo-responsive azobenzene group can envelope the chiral "centre" like "closing petals" using terminal alkyl tails and induce the decreased dihedral angle of binaphthol moiety during *E*→Z isomerization. The reported single-molecular binary photoswitch in this work can control the supramolecular chirality "1/0" of the whole system, and we are now working on developing advanced LC optics.

## Experimental Section

**Materials:** All the chemicals were provided by Sigma-Aldrich without any further purity. Vertically aligned polyimide (PI; DL-4018) was purchased from Shenzhen Dalton Electronic Materials Coo., Ltd.. And all organic solvents were analyticly pure, and dried or redistilled before using. For column chromatography, silica gel (Silicycles Siliaflash P60, 40-60 μm, 230-400 mesh) was used in all cases. Separation was carried out on silica gel 60 (silicon dioxide, $SiO_2$; Merk, Germany) and kieselguhr $F_{254}$ (celite; Merk, Germany) for thin-layer chromatography (TLC), and visualization was accomplished by stain.

In Grandjean-Cano wedge method, the wedge cells (KCRK-07, tan$\theta$ = 0.0196) were provided by Japan EHC Co., Ltd.. For the generation of the planar anchoring, a glass substrate was thoroughly cleaned and spin-coated with PI alignment layer. Another cover glass plate was sticked together with the spacing distance of 5 μm fixed by the UV-curing spacer (Suzhou Nanomicro Technology Co., Ltd), to construct the LC cell.

**Synthesis:** The target molecule, [1,1'-binaphthalene]-2,2'-diyl bis(3,5-bis((E)-(4-(hexyloxy)phenyl)diazenyl)benzoate), was synthesized in a five-step process as shown in **Scheme 1**. All the detailed procedures are given below.

**(a) Synthesis of methyl 3,5-diaminobenzoate (2):** 3,5-Diaminobenzoic acid (10 g, 65 mmol) and sulfuric acid (5 mL) were mixed in methanol (75 mL). The solution was heated at reflux overnight. After the mixture was cooled down to room temperature, the solvent was removed by rotary evaporation. The residue was diluted with 50 mL of ultrapure water. Afterward, the solution was neutralized with saturated sodium carbonate ($Na_2CO_3$) solution. The product was extracted twice from the aqueous phase with ethyl acetate (100 mL). Anhydrous sodium sulfate ($Na_2SO_4$) powders were added to dry the organic phase and then removed by filtration. Ethyl acetate was removed under vacuum to yield 2 as light-yellow solid (10 g, 50 mmol; 76%).

**(b) Synthesis of methyl 3,5-bis((E)-(4-hydroxyphenyl)diazenyl)benzoate (3):** Methyl 3,5-diaminobenzoate (2) (5 g, 25 mmol) was dissolved in an aqueous solution of diluted hydrochloric acid (HCl; 0.75 M, 80 mL). After cooled to 0 °C, the resulting solution was gradually mixed with 16 mL of iced solution of sodium nitrite ($NaNO_2$; 4.5 g, 65 mmol) by dropwise addition. Subsequently, the obtained brown diazotized mixture was added dropwise into a mixture of phenol (11.32 g, 120 mmol), NaOH (4.8 g, 120 mmol) and water (150 mL) at 0 °C for coupling. The crude product was neutralized with HCl (1 M) aqueous solution, and then filtered and washed with distilled water. The final orange-red product was pufified by column chromatography ($SiO_2$, pentane/EA=1:3), to yield 3 as orange-red solid (1.22g, 3.25 mmol; 13%)

**(c) Synthesis of methyl 3,5-bis((E)-(4-(hexyloxy)phenyl)diazenyl)benzoate (4):** 1.22 g (3.25 mmol) of the orange-red precipitate (3) was added to a mixture of potassium carbonate ($K_2CO_3$; 2.01 g, 14.5 mmol), bromohexane (1.2g, 7.2 mmol) and tetrabutylammonium iodide (TBAI; 0.3 g, 0.8 mmol) in 30 mL of acetonitrile at nitrogen atmosphere. The reaction mixture was heated at reflux overnight. After cooled down to room temperature, the organic layer of the mixture was filtrated. After the removal of solvent, the residue was dissolved in dichloromethane (DCM). The organic phase was washed three times with brine, dried with anhydrous $Na_2SO_4$ powders, and concentrated under reduced pressure. The obtained orange oil was purified by column chromatography ($SiO_2$, pentane/DCM=2:1). The solvent was removed in vacuum to yield 4 as a yellow solid (870 mg, 1.63 mmol; 50%).

**(d) Synthesis of 3,5-bis((E)-(4-(hexyloxy)phenyl)diazenyl)benzoic acid (5):** Compound 4 (130 mg, 0.238 mmol) was hydrolyzed in the mixed solution of sodium hydroxide (NaOH; 0.26 M, 6 mL), tetrahydrofuran (THF; 10 mL) and methanol (10 mL) by vigorous stirring at reflux, and the process was monitored with TLC. After cooled down to room temperature, the mixture was neutralized with HCl (1 M) aqueous solution. After removal of the organic solvent under reduced pressure, 20 mL of DCM was added. The organic layer was seperated . Compound 5 was obtained as a red solid after removal of the organic solvent. The crude product was used without further purification.

**(e) Synthesis of [1,1'-binaphthalene]-2,2'-diyl bis(3,5-bis((E)-(4-(hexyloxy)phenyl)diazenyl)benzoate) (1):** A solution of compound 5 (125 mg, 0.235mmol) in chloroform (20 mL) was added to the mixture of (R)-(+)-1,1'-bi-2-naphthol (33.4 mg, 0.117 mmol), dicyclohexylcarbodiimide (DCC; 60.56 mg, 0.294 mmol) and 4-dimethylaminopyridine (DMAP; 8.9 mg, 0.0735 mmol) under the protection of dry argon. The mixture was stirred at room

temperature overnight. After removal of the solvent, the residue was purified by column chromatography ($SiO_2$, pentane/DCM=2:3). The organic solvent was removed in vacuum to yield 1 as a red solid (40 mg, 0.035 mmol; 30%).

**Characterizations:** $^1$H-NMR spectra were recorded on a Varian AMX-500 (500 MHz), a Varian AMX-400 (400 MHz). Kinetic and concentration-dependent $^1$H-NMR studies were recorded on a Varian AMX-500 (500 MHz) in dichloromethane-d ($CD_2Cl_2$). The corresponding chemical shifts were reported in δ values (ppm) relative to deuterochloroform ($CDCl_3$; $^1$H δ=7.25, $^{13}$C δ=77.2): $^1$H δ=5.32, $^{13}$C δ=54. For $^1$H-NMR, the signals were assigned as following: singlet (s), doublet (d), double doublet (dd), triplet (t), quartet (q) and multiplet (m).

Proton magnetic resonance spectroscopy (HMRS) was measured using a double focusing high-resolution mass spectrometer (MS-902, AEI). Ultraviolet-visible (UV-Vis) spectra were obtained with JASCO V-630 spectrophotometer in a 1 cm quartz cuvette at room temperature. Solution circular dichroism (CD) spectra were recorded on a JASCO J-715 spectropolarimeter at room temperature. For all the details of the structural information and spectra, see the attached supporting information.

Irradiation experiments were performed using an ENB-280C/FE lamp (Model series, Spectroline) at 365 nm (± 30 nm). All the optical phenomena of CLC mixture were observed and recorded *via.* polarizing optical microscope (POM; DM2700p, Leica).

Measurement of helical twisting power (HTP) HTP value and its changes upon photoirradiation were determined by Grandjean-Cano method. The definition of HTP is: β = 1 / (pc), where p is the helical pitch and c is the molar or mass concentration. The pitch was determined by: p = 2R tanθ, where R represents the distance between the disclination lines and θ is the wedge angle of the wedge cells (tan θ =0.0196). The LC mixtures were prepared by doping compound 1 into E7 and then filled into the wedge cells by capillary force. The wedge cells were heated to 70 ℃ then cooled down to room temperature with a cooling rate of -1 ℃·min$^{-1}$. The disclination lines were observed through POM. The length of R was measured as the intervals between the disclination lines to calculate out the pitch. Two different mass concentrations (wt. %) were used for the dopant, and the HTP was determined by plotting 1/p (μm$^{-1}$) against concentration of the dopant (see **Figure S5**).

## Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 51773069, 51703070, and 21809095), Guangdong Provincial Key Laboratory of Optical Information Materials and Technology (Grant No. 2017B030301007), Science and Technology of Guangdong Province (No. 2018B030306031), Science and Technology Program of Guangzhou (No. 2019050001), Startup funding from South China Normal University (No. 850134 and 8S0474), MOE International Laboratory for Optical Information Technologies and the 111 Project. All the calculation and modelling were supported by Chem Cloud Computing of Beijing University of Chemical Technology.

**Keywords:** azobenzene • chirality • host-guest systems • liquid crystals • photoswitches

## References

[1] M.Liu, Z.Li, T.Wang. *Chem. Rev.* **2015**, *115,* 7304.
[2] L.Zhang, T.Wang, Z.Shen, M. Liu, *Adv. Mater.* **2016**, *28*, 1044–1059.
[3] S.M.Morrow, A.J.Bissette, S.P.Fletcher, *Nat. Nanotechnol.* **2017**, *12*, 410.
[4] Z.Lv, Z.Chen, K.Shao, G.Qing, T.Sun, *Polymers*. **2016**, *8*, 310.
[5] Q.Li, L.Li, J.Kim, H.-s.Park, J.Williams, *Chem. Mater*. **2005**, *17*, 6018–6021.
[6] S.W.Choi, H.Takezoe, *Soft Matter*. **2016**, *12*, 7937–7942.
[7] L.Qin, W.Gu, J.Wei, Y.Yu, *Adv. Mater.* **2018**, *30*, 1704941.
[8] C.Ruslim, K.Ichimura, *J. Mater. Chem*. **2002**, *12*, 3377–3379.
[9] M.Kawamoto, T.Aoki, T. Wada, *Chem. Commun.* **2007**, 930–932.
[10] Y.Wang, A. Urbas, Q.Li, *J. Am. Chem. Soc.* **2012**, *134*, 3342–3345.
[11] S.Iamsaard, S.J.Aßhoff, B.Matt, T.Kudernac, J.J.Cornelissen, S.P.Fletcher, N.Katsonis, *Nat. Chem.* **2014**, *6*, 229.
[12] H.Nishikawa, D.Mochizuki, H.Higuchi, Y.Okumura, H.Kikuchi, *ChemistryOpen*. **2017**, *6*, 710–720.
[13] H.Wang, H.K.Bisoyi, L.Wang, A.M.Urbas, T.J.Bunning, Q.Li, *Angew. Chem. Int. Ed.* **2018**, *57*, 1627–1631.
[14] L.Yin, Y.Zhao, S.Jiang, L.Wang, Z.Zhang, J.Zhu, W.Zhang, X.Zhu, *Polym. Chem*. **2015**, *6*, 7045–7052.
[15] Y.Cai, Z.Guo, J.Chen, W. Li, L.Zhong, Y.Gao, L.Jiang, L.Chi, H.Tian, W.H.Zhu, *J. Am. Chem. Soc.* **2016**, *138*, 2219–2224.
[16] Li Y., Urbas A., and Li Q. J. Am. Chem. Soc. **2012**, 134, 9573–9576.
[17] Y.Li, C.Xue, M.Wang, A. Urbas, Q. Li, *Angew. Chem. Int. Ed*. **2013**, *52*, 13703–13707.
[18] D.Zhao, L.T.Van, J.Cheng, B.L.Feringa, *Nat. Chem.* **2017**, *9*, 250–256.
[19] T.Ikeda, *J. Mater. Chem.* **2003**, *13*, 2037–2057.
[20] X.P.Tan, Z. Li, M.Xia, X.H.Cheng, *RSC Adv*. **2016**, *6*, 20021–20026.
[21] M.Goh, J. Park, Y.D. Han, S. Ahn, K.Akagi, *J. Mater. Chem.* **2012**, *22*, 25011–25018.
[22] M.Goh, K.Akagi, *Liq. Cryst.* **2008**, *35*, 953–965.
[23] S.Pieraccini, S.Masiero, G.P.Spada, G.Gottarelli, *Chem. Commun*. **2003**, 598–599.
[24] Y.Kim, N.Tamaoki, *ACS Appl. Mater. & Interfaces*. **2016**, *8*, 4918–4926.
[25] G.Gottarelli, G.P.Spada, R.Bartsch, G.Solladie, R.Zimmermann, *J.Org. Chem.* **1986**, *51*, 589–592.
[26] G.Gottarelli, M.Hibert, B.Samori, G.Solladie, G.P.Spada, R.Zimmermann, *J. Am. Chem. Soc*. **1983**, *105*, 7318–7321.
[27] C.Rosini, I.Rosati, G.P.Spada, *Chirality*.**1995**, *7*, 353–358.
[28] J.Ma, Y.N.Li, T. White, A. Urbas, Q.Li, *Chem. Commun*. **2010**, *46*, 3463–3465.
[29] T.Yoshioka, T.Ogata, T. Nonaka, M.Moritsugu, S.N. Kim, S.Kurihara, *Adv. Mater.* **2005**, *17*, 1226–1229.
[30] R.Thomas, Y.Yoshida, T.Akasaka, N.Tamaoki, *Chem.Eur. J.* **2012**, *18*, 12337–12348.
[31] T.J.White, A.D.Zhao, S.A.Cazzell, T.J.Bunning, T. Kosa, L.Sukhomlinova, T.J.Smith, B. Taheri, *J. Mater. Chem.* **2012**, *22*, 5751–5757.
[32] T.van Leeuwen, T.C. Pijper, J.Areephong, B.L.Feringa, W.R.Browne, N.Katsonis, *J. Mater. Chem.* **2011**, *21*, 3142–3146.
[33] Y.N.Li, M.F.Wang, A. Urbas, Q. Li, *J. Mater. Chem. C*. **2013**, *1*, 3917–3923.
[34] T.Yamaguchi, T.Inagawa, H.Nakazumi, S.Irie, M.Irie, *J. Mater. Chem.* **2001**, *11*, 2453–2458.
[35] N.Kim, H.Lam, T.Kyu, *J. Phys. Chem. B*. **2010**, *14*, 16381–16387.
[36] R.Eelkema, B.L.Feringa, *Chem.Asian J.* **2006**,*1*, 367–369.
[37] R.A.van Delden, N.Koumura, N.Harada, B.L.Feringa, *Proc. Natl. Acad. Sci. U. S. A.* **2002**,*99*, 4945–4949.
[38] J.-a.Lv, Y.Liu, J.Wei, E.Chen, L.Qin, Y. Yu, *Nature*.**2016**, *537*, 179–184.
[39] H.K.Bisoyi, Q. Li, *Acc. Chem. Res*. **2014**, *47*, 3184–3195.

[40] N.Koumura, R.W.J.Zijlstra, R.A.van Delden, N.Harada, B.L.Feringa, *Nature*.**1999**,*401*, 152–155.

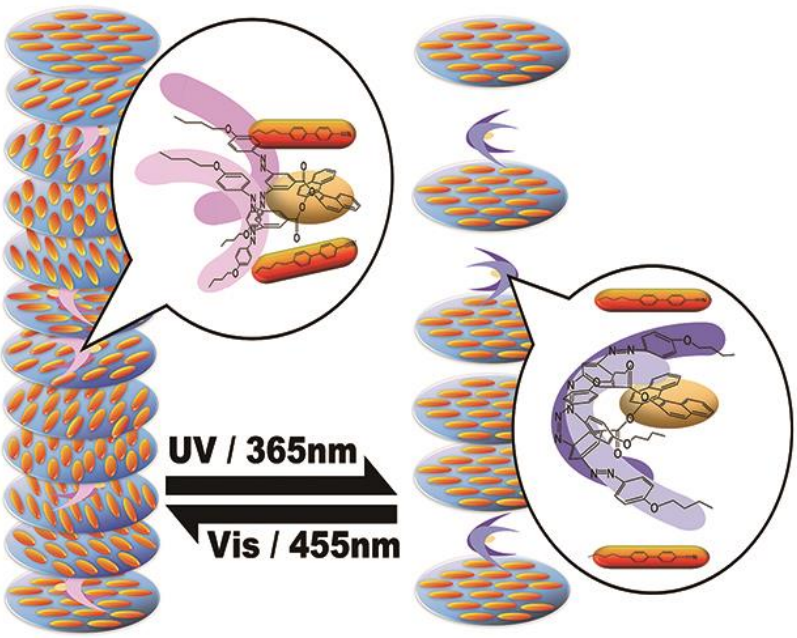
[41] H.Hayasaka, T. Miyashita, M.Nakayama, K. Kuwada, K.Akagi, *J. Am. Chem. Soc.* **2012**, *134*, 3758–3765.

[42] K.Watanabe, Z.Sun, K. Akagi, *Chem. Mater.* **2015**, *27*, 2895–2902.

[43] A.R.Campanelli, A.Domenicano, F.Ramondo, *J. Phys. Chem. A.* **2012**, *116*, 8209–8217.

[44] G.De Luca, J.W.Emsley, A. Lesage, D.Merlet, *Liq. Cryst.* **2012**, *39*, 211–219

# Table of Contents




**Please ensure an appropriate text (60-80 words).**

Upon ultraviolet light-induced isomerization, terminal alkyl tails of flower-like azobenzene compound envelop the chiral “centre” with decreasing dihedral angle of the binaphthol moiety, like “closing petals”. This variation in hierarchical conformation prevents from transferring charity from the guest molecule to the host liquid crystal matrix, resulting in a supramolecular chirality 0. And the transition is reversible under visible light irradiation.