Chapter 2

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

**Abstract:** Chiral supramolecular assemblies are abundant in nature, but controlling the chirality of artificial systems remains a challenge. In this work, we developed a system where supramolecular chirality can be controlled between chiral and achiral states, namely a chiral “1/0” switch using a flower-like azobenzene compound with a binaphthol core. Upon photo-isomerization by ultraviolet irradiation, the terminal alkyl tails envelop the chiral “center” with a reduction in the dihedral angle of the binaphthol moiety from 76.1° to 61.4°, like “closing petals”. In the doped liquid crystal E7 matrix, this hierarchical conformational transition prevents the transfer of chirality to the host liquid crystal, resulting in a degradation from cholesteric phase (HTP value: 13.84 μm⁻¹) to an achiral nematic phase.
2.1 Introduction

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

There are two key issues for supramolecular chirality: (1) chirality transfer from the molecular scale to macroscopic scale; (2) control of chirality for modulating macroscopic properties. In particular, the latter is viewed as an important challenge. Due to complexity and flexibility of noncovalent interactions, it is difficult to change the selfassembly via direct conformational control of chiral units inside the supramolecular system. Some external stimulus 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 accuracy and non-invasive nature. In most cases, light-responsive molecular machines, whose conformational transformation can be active by light irradiation, are introduced into chiral supramolecular systems as an actuator to control their helicity, morphology or motility. Among all these light-controlled chiral supramolecular systems, dynamic control of supramolecular chirality in liquid crystal seems to be the most interesting one, because it is highly related to optical properties in devices, e.g. reflected color tuning, circular polarized luminescent switching and control of light direction. In cholesteric liquid crystal phase, direct helix inversion from left- to right-handed and out of equilibrium phase tuning have been achieved. However, chiral on–off switching of the whole supramolecular liquid crystal system induced by light are still with few examples.
In this work, we designed and synthesized a flower-like binaphthyl compound bearing azobenzene moieties, 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 “center”, 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 “blossom”, similar to the opuntia flower in day and night, and the chirality of the LC system is regained.

2.2 Results and Discussion

In this work, we integrated a chiral moiety and photosensitizer in one compound to form a flower-like photo-controllable switch. For the choice of chiral moiety, cholesterol\textsuperscript{34} and binaphthyl\textsuperscript{35} derivatives are two mostly used moieties. As reported previously, binaphthyl derivatives can induce large helical twisting power (HTP, $\beta$) value up to hundreds $\mu$m\textsuperscript{-1}\textsuperscript{36,37} and behaved much better than cholesterol-modified azobenzenes\textsuperscript{38}. In the molecular structures of these binaphthyl derivatives, steric hindrance may induce the carbon–carbon bridged bond between 1 and 1’ position rotating to form different dihedral angles ($\theta$) of the two naphthyl rings, and induce some changes in helical structure and therefore affect the HTP value\textsuperscript{39–41}. As chromophore moiety, the selected azobenzene\textsuperscript{42–44} is more commonly used than fulgides,\textsuperscript{45} diarylethenes,\textsuperscript{46–48} spiropyrans,\textsuperscript{49} and other photochromic moieties.\textsuperscript{50,51} It can rapidly undergo trans–cis isomerization by ultraviolet (UV) exposure (365 nm), to change the helical twisting power (HTP, evaluated by $\beta$ value) of the host LC system.\textsuperscript{52–54} We introduced four photochromic azobenzene groups on both sides of the binaphthyl center, to form a highly symmetric and flower-like dopant (i. e. compound 1 in Scheme 2.1) for the control of the supramolecular chirality of LC system.
Scheme 2.1 Synthetic route of compound 1.

2.2.1 UV-Vis Spectroscopic Study

Photochemical properties of compound 1 were characterized in dimethyl sulfoxide (DMSO) solution by UV-Vis spectroscopy. Figure 2.1 A showed a strong absorption band with a maximum absorption wavelength ($\lambda_{\text{max}}$) 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 2.1 B), which is a characteristic behavior of the azobenzene compounds. The variation in absorbance at 360 nm was repeated three times via alternating irradiation with 365 and 455 nm light (see Figure 2.1 C). The photochemical switching process can be reproduced several times without significant fatigue.
2.2.2 ¹H-NMR Spectroscopic Study

The switching process of compound 1 was monitored by ¹H-NMR spectroscopy in CD₂Cl₂ as well (see Figure 2.2 A). 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. Hₐ in Figure 2.2 A) shifted upfield to 3.95 ppm under UV irradiation (see Figure 2.2 B). The integrals of the Hₐ 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 2.2 C). The incomplete Z→E switch may attribute to the above-mentioned fatigue of UV absorbance.

**Figure 2.2** (A) 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. (500 MHz; 298 K; CD$_2$Cl$_2$) Enlarged views of partial $^1$H-NMR spectra (500 MHz; 298 K; CD$_2$Cl$_2$): (B) PSS mixture of E-1 after irradiated at 365 nm for 1.5 hours, and (C) PSS mixture of Z-1 after irradiated at 455 nm for 1.5 hours.

### 2.2.3 Kinetic Analyses

By Eyring plot analysis, the activation parameters for thermal cis-trans (Z→E) inversion of compound 1 were obtained (see Figure 2.3): the enthalpy of activation ($\Delta H$) is 165.73 kJmol$^{-1}$ and the entropy of activation ($\Delta S$) is 187.08 Jmol$^{-1}$K$^{-1}$. According to Gibbs equation, the free energy of activation ($\Delta G$) at 293.15 K is 110.89 kJmol$^{-1}$ and correspond to a half-life of the thermal step at 293.15 K (i. e. 20 °C) 1817.2 hours. It demonstrates that the Z isomers of compound 1 is very stable at room temperature.
Kinetic studies of the thermal inversion step from Z to E isomers by UV-Vis absorption spectral changes at 365 nm at 4 different temperatures conditions in DMSO (45 °C, 50 °C, 55 °C and 60 °C).

2.2.4 CD Spectroscopic Study

The switching process of compound 1 was investigated by CD spectroscopy as depicted in Figure 2.4 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 center. 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 2.2 C. But the unavoidable molecular fatigue still hinders complete conformational recovery (Figure 2.4).
Figure 2.4 (A) Experimental CD spectra of E-1 and Z-1 isomers of compound 1 in DCM and (B) related CD signal-changing curve at 321 nm upon alternating irradiation of 365 and 455 nm light with every irradiation period of 3 minutes.

2.2.5 Concentration Dependence

Compound 1 was prepared as a series of solution ranging from 40 to 2.5 mmol · L⁻¹ and all the chemical shifts of ¹H-NMR signals remain unchanged (see Figure 2.5 A), indicating no self-aggregation. Similarly, UV absorbance at 365 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.

Figure 2.5 (A) ¹H-NMR spectra (500 MHz, 298 K, CD₂Cl₂) and (B) UV absorbances of compound 1 with different concentration (365 nm, DCM).
2.2.6 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 ($\beta$) of compound 1 and its changes under photoirradiation were determined by the Grandjean-Cano method. By measurement, the initial value of HTP in weight percentage in cholesteric E7 is 13.84 μm$^{-1}$. Once UV light was irradiated for one hour, all the stripes completely disappeared (see Figure 2.6 A). It indicates that the cholesteric phase of E7 change into nematic phase. This change can be ascribed to the trans-cis ($E \rightarrow Z$) isomerization of the azobenzene moieties. Reversibly, when Vis light was irradiated for one hour, these stripes reappeared and the measured HTP was 10.95 μm$^{-1}$. The recovered $\beta$ 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. 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 2.6 B, 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 ($Z \rightarrow E$) isomerization upon Vis irradiation.
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Figure 2.6 (A) Color change 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) 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.

2.2.7 Mechanistic Analyses

In order to study the mechanism in more detail, we performed DFT calculations to simulate the conformational change of compound 1 (Figure 2.7). The naphthalene and two side azobenzene branches were entitled as three vertexes of triangle shape, respectively. The original symmetrical compound 1 acts like a blossoming “quatrefoil” with the “center” dihedral angle of 76.1°. When UV light irradiates, the symmetric 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 “center” like “closing petals”. At the same time, the dihedral angle between two naphthalene ring decreases to a smaller angle of 61.4°.
2.3 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 properties, e.g. reflectivity, can be reversibly switched by photoirradiation.

According to computational simulation and molecular geometry optimization, the photo-responsive azobenzene group can envelope the chiral “center” like “closing petals” using terminal alkyl tails and induce the decreased dihedral angle of binaphthol moiety during $E \rightarrow Z$ isomerization. The reported single-molecular binary
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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.

2.4 Experimental Section

2.4.1 Materials

All the chemicals were purchased from Sigma-Aldrich. Vertically aligned polyimide (PI; DL-4018) was purchased from Shenzhen Dalton Electronic Materials Co., Ltd. All organic solvents were analytically 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, SiO2; Merck, Germany) and kieselguhr F254 (celite; Merck, Germany) for thin-layer chromatography (TLC), and visualization was accomplished by stain.

2.4.2 Characterization

$^1$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$_2$ (CD$_2$Cl$_2$). 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; CD$_2$Cl$_2$; $^1$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. Irradiation experiments were performed using an ENB-280 C/FE lamp (Model series, Spectroline) at 365 nm ($\pm$30 nm). All the optical phenomena of CLC mixture were observed and recorded via polarizing optical microscope (POM; DM2700p, Leica).The wedge cells (KCRK-07, tanθ=0.00785) were provided by Japan EHC Co., Ltd. For the generation of the planar...
anchoring, a glass substrate was thoroughly cleaned and spin-coated with polyimide alignment layer. The coated substrate was rubbed with velvet in a certain direction. Another cover glass plate was sticked together with the spacing distance of 5 μm fixed by the UV-curing spacer to construct the LC cell.

2.4.2 Synthesis

The target molecule, \([1,1'-\text{binaphthalene}]\)-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.

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\(_2\)CO\(_3\)) solution. The product was extracted twice from the aqueous phase with ethyl acetate (100 mL). Anhydrous sodium sulfate (Na\(_2\)SO\(_4\)) 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%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 6.78 (d, J = 1.9 \text{ Hz}, 2\text{H}), 6.19 (s, 1\text{H}), 3.86 (s, 3\text{H})\).

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 purified by column chromatography (SiO\(_2\), pentane/EA=1:3), to yield 3 as orange-red solid (1.22 g, 3.25 mmol; 13%). \(^1\)H
NMR (400 MHz, CDCl₃) δ 8.61 (d, J = 1.9 Hz, 1H), 8.53 (d, J = 1.8 Hz, 1H), 7.95 (d, J = 8.8 Hz, 3H), 6.98 (d, J = 8.8 Hz, 4H), 5.37 (s, 2H), 4.02 (s, 3H).

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 (K₂CO₃; 2.01 g, 14.5 mmol), bromohexane (1.2 g, 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 Na₂SO₄ powders, and concentrated under reduced pressure. The obtained orange oil was purified by column chromatography (SiO₂, pentane/DCM=2:1). The solvent was removed in vacuum to yield 4 as a yellow solid (870 mg, 1.63 mmol; 50%).

H NMR (400 MHz, CDCl₃) δ 8.60 (d, J = 1.7 Hz, 2H), 8.73 – 8.50 (m, 3H), 8.53 (s, 1H), 7.98 (d, J = 8.9 Hz, 5H), 7.98 (d, J = 8.9 Hz, 4H), 7.03 (d, J = 8.9 Hz, 6H), 7.03 (d, J = 8.9 Hz, 5H), 4.07 (t, J = 6.5 Hz, 5H), 4.17 – 3.94 (m, 12H), 4.01 (s, 4H), 1.91 – 1.61 (m, 7H), 1.88 – 1.79 (m, 5H), 1.61 – 1.50 (m, 8H), 1.60 – 1.49 (m, 8H), 1.00 (t, J = 7.4 Hz, 8H), 1.00 (t, J = 7.4 Hz, 7H).

C NMR (126 MHz, Chloroform-d) δ 171.6, 171.5, 169.0, 164.9, 156.2, 149.3, 134.6, 131.7, 127.8, 127.7, 124.1, 124.0, 122.4, 117.4, 106.1, 105.7, 105.5, 71.1, 55.1, 34.2, 31.8, 28.3, 25.2, 16.7. HRMS (ESI) calcd for C₃₂H₄₀N₄O₄ 545.3122 (M+), found 545.3106.

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 separated. Compound 5 was obtained as a red solid after removal of the organic solvent. The crude product was used without further purification.
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, 0.235 mmol) 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 (SiO2, pentane/DCM=2:3). The organic solvent was removed in vacuum to yield 1 as a red solid (40 mg, 0.035 mmol; 30%). $^1$H NMR (500 MHz, CD$_2$Cl$_2$) $\delta$ 8.47 (s, 1H), 8.30 (d, $J$ = 1.2 Hz, 2H), 8.06 (d, $J$ = 9.0 Hz, 2H), 7.96 (dd, $J$ = 12.9, 8.8 Hz, 10H), 7.69 (d, $J$ = 8.9 Hz, 2H), 7.52 (d, $J$ = 7.9 Hz, 2H), 7.46 (d, $J$ = 9.5 Hz, 5H), 7.05 (d, $J$ = 8.8 Hz, 8H), 4.09 (t, $J$ = 6.5 Hz, 9H), 1.97 – 1.76 (m, 9H), 1.53 (s, 5H), 1.45 (t, $J$ = 27.4 Hz, 22H), 0.97 (t, $J$ = 6.6 Hz, 13H). $^{13}$C NMR (126 MHz, Methylene Chloride-d2) $\delta$ 149.7, 149.1, 136.0, 134.4, 133.8, 132.5, 130.8, 129.5, 128.7, 128.5, 127.8, 127.7, 126.2, 124.2, 122.5, 122.0, 117.4, 116.8, 104.2, 103.7, 103.7, 103.2, 103.2, 103.2, 102.7, 101.8, 101.7. HRMS (ESI) calcd for C$_{82}$H$_{86}$N$_8$O$_8$ 1311.6641 (M+), found 1311.6626.

2.4.4 Measurement of helical twisting power (HTP)

HTP value and its changes upon photoirradiation were determined by Grandjean-Cano method. The definition of HTP is: $\beta=1/(pc)$, where $p$ is the helical pitch and $c$ is the molar or mass concentration. The pitch was determined by: $p=2R \tan\theta$, where $R$ represents the distance between the disclination lines and $\theta$ is the wedge angle of the wedge cells ($\tan \theta=0.00785$). 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°C then cooled down to room temperature with a cooling rate of -1°C 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. In this case, two different mass concentrations (wt.%.) were used for the dopant.
2.5 Reference