Photoresponsive molecular motors and switches in liquid crystal materials

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Chapter 6

A Red-light Based Donor-Acceptor Stenhouse Adduct in Liquid Crystal
Abstract
Here we report a novel chiral Donor-Acceptor Stenhouse Adduct based red-light-driven switch which exhibits reversible isomerization from an acyclic triene to a cyclopentenone isomer. The DASA switch shows full conversion from the ring open form to the ring closed form accompanied by color change from intense blue to transparent. By doping the molecule to nematic liquid crystals (E7), the chiral switchable dopant is able to induce a cholesteric phase. The reflection color of the photoresponsive cholesteric phase can be tuned by red light irradiation (617 nm) and the original state is recovered by thermal back switching.
6.1 Introduction

Dynamic tuning the self-organized structure of liquid crystals has received extensive attention in recent years. In particular, precise control the optical properties of cholesteric liquid crystals (CLCs) has enable several remarkable applications, such as color display, laser tuning, one- and two-dimensional beam steering and circular polarized light reflection. CLCs are usually fabricated by introducing covalently or non-covalently chiral molecules into an achiral nematic liquid crystal host and the helical pitch is a significant parameter to determine the reflection band of CLCs. The key challenge is to dynamically control the helical pitch as it allows the manipulation of the helical structure and optical properties in CLCs. There are several practical methods to dynamical control the helical pitch of CLCs, such as the use of electricity, pressure and light. Among those stimuli, light appears to be attractive, as it can provide a non-invasive approach to modulating CLCs spatially, temporally and precisely. Introduction of photo-responsive chiral molecules as chiral dopants has resulted in various CLCs systems in which the helical pitch can be easily tuned by light. Overcrowded alkene based chiroptical switches, azobenzene derivatives and diarylethene derivatives are the most widely used switches in photo-responsive chiral dopants. These switchable molecules can isomerize between 2 chiral states upon UV-light irradiation and therefore change the self-organized structures of the CLCs and helical pitch when they are used as chiral dopants in the nematic LC. For example, an azobenzene derivatives was first reported to be able to tune the reflective color in CLCs from green to red upon UV light irradiation by Sackmann in 1971. Chiroptical switches were first applied in LC material in 1995, and upon UV and blue light irradiation, LC material shown reversible interconversion between nematic and cholesteric phases. However, UV light is not favorable for devices and commercial application, as it usually has disadvantages, such as decomposition of the materials, poor penetration through the substrate (e.g., glass or plastic), strong absorption by the substrate that lead to local over-heating, etc. Therefore, designing a visible light or red light driven chiral switch
as a chiral dopant has been a major challenge and might boost the development of advanced LC devices.

To achieve the visible or red light–responsive capability, many approaches have been focused on functionalization of azobenzenes. Successful examples include the introduction of methoxy, \textsuperscript{33-36} fluorine, \textsuperscript{37,38} chlorine, \textsuperscript{39-41} and other groups.\textsuperscript{42-44} However, lengthy synthesis , low photostationary state or low solubility make the above-mentioned systems less interested. Apart from azobenzenes, Donor-Acceptor Stenhouse Adducts (DASAs), which is a new class of negatively photochromic photoswitches, are known to absorb visible light (530-670 nm)\textsuperscript{45-48}. Upon visible light irradiation, DASAs are able to change from a strong colored elongated triene isomer to a colorless cyclopentenone isomer. The large geometrical change upon visible light irradiation makes it a potential suitable candidate for dynamic tuning the self-organized structure of CLCs as a chiral dopant.

There are two approaches to tune the helicity in cholesteric phase by molecular switches and motors; (i) UV light driven molecular motors which contains intrinsic chirality \textsuperscript{16,21,22} (Figure 6.1 A) or (ii) photoresponsive molecular switches that covalently connected to chiral moieties \textsuperscript{49} (Figure 6.1 B). In the present study, we report the design and synthesis of a red light driven DASA-BINOL and its use as a chiral dopant in liquid crystal. Upon red light (617 nm) irradiation, intermolecular interaction between DASA and the liquid crystal (E7) are modulated and therefore the helical pitch of CLCs can be changed accordingly, accompanied by the change of reflective wavelength of the devices at the same time (Figure 6.1 C).
Figure 6.1 Light responsive chiral dopants. (a) UV light driven chiral dopant based on overcrowded alkene and its switching upon UV light irradiation (b) Green light driven chiral dopant and its switching upon green light irradiation. (c) Design of photoswitchable DASA-BINOL and its use as a chiral dopant in liquid crystal. The helical pitch changes upon red light irradiation.

6.2 Result and discussion

6.2.1 Design and Synthesis

The light-driven switch DASA-BINOL used for this work consist of two essential parts: (a) (R)-Binol which provides the molecule with chirality; (b) a photoresponsive DASA unit which enables the light-responsive properties of the whole molecule (Scheme 6.1). The maximum absorption of DASA can be shifted to the red light region (615 nm) by employing barbituric acid as the “acceptor” and indoline as the “donor”\(^4\). In this design, we have attached an (R)-Binol to the indoline as an intrinsic chiral “donor”. The “donor” was prepared as shown in Scheme 6.1. Indole was first reduced by NaBH\(_3\)CN and the amine was protected with a “Boc” group, following the treatment of Bis(pinacolato)diboron to replace the bromo with a borate ester to obtain indoline 7 (see experimental section). Suzuki coupling was performed to covalently attached (R)-Binol to the indole core. The “Boc” group was removed by...
treatment using strong acid (TFA) at room temperature after coupling. In the final step, target molecule **DASA-BINOL** was prepared by Knoevenagel condensation with furfural derivative **10** by adding 1 equivalent of **indoline 9**. The details of the synthesis and purification of **DASA-BINOL** and characterization can be found in the experimental section.

![Scheme 6.1 Partial synthetic route of DASA-BINOL.](image)

### 6.2.2 $^1$H-NMR studies

Figure 6.2 shows the photoisomerization process using $^1$H-NMR spectroscopy for analysis of the designed molecule. Upon red light (617 nm) irradiation **DASA-BINOL** undergoes a ring closure step (Figure 6.2 B). In order to characterize the cyclization process, a solution of **DASA-BINOL** in CD$_2$Cl$_2$ was irradiated in situ with a 617 nm LED through an optical fiber and the $^1$H-NMR spectrum was recorded every 10 min until no further changes were observed. Before irradiation, the sample was stored in the dark for 1 h at rt to achieve dark equilibrium, resulting in 60% of the ring closed isomer **C-11** and 40% of ring open isomer **O-11** (Figure 6.2 B). Upon light irradiation, the characteristic protons at 12.44 (e), 7.82 (a), 7.74 (d), 6.79 (c), 6.24 (b) ppm, which are the vinyl protons, gradually disappeared and the intensity of absorption at 7.79 (c’), 6.44 (b’), 5.35 (a’), 4.17 (c’) and 3.81(d’) ppm enhanced, which can be attributed to the formation of the ring closed cyclopentenone **C-11** (Figure 6.2 A). All the ring open isomers converted to ring closed isomers within 1 h.
irradiation at 617 nm. When **DASA-BINOL** was dissolved in methanol, only the cyclized form can be observed (SI Figure 6.12), which indicates the equilibrium between open and closed form is solvent dependent.

**Figure 6.2** (a) $^1$H-NMR spectrum of **DASA-BINOL** before (blue curve) and after (red curve) 617 nm light irradiation at 0 °C for 1 h in CD$_2$Cl$_2$ ($5 \times 10^{-3}$ M) (b) Photoisomerization of **DASA-BINOL**.

### 6.2.2 UV-Vis studies

Next, the photochromic properties of **DASA-BINOL** were studied by both UV-Vis and fluorescence spectroscopy in DCM. Before measurement, the sample was stored in dark for 1 h at rt to achieve a dark equilibrium. The absorption bands of **DASA-BINOL** were observed at 310 nm and 626 nm (Figure 6.3 A). Upon irradiation at 617 nm, the absorption at 626 nm gradually decreased until fully disappearance while the absorption at 310 nm showed an increase due to the reversible thermal 4π electrocyclic reaction. The isosbestic point at around 340 nm indicates the single molecular switching behavior of **DASA-BINOL** (Figure 6.3 A). In the thermal back switching, DASA undergoes a isomerization from PSS to half way to dark equilibrium state.$^{50,51}$ In this study, we have followed the recovery process by monitoring the absorption at $\lambda_{\text{max}} = 626$ nm (SI Figure 6.5). During the first cycle, data points were recorded every 60 s, and the detailed plot shown that the absorption at 626 nm recovered back from PSS to dark equilibrium with a life-time of 32 min at 25 °C. To study fatigue resistance properties, the solution sample was irradiated (DCM, 617 nm) and allowed to thermally relax at 25 °C for 5 cycles (Figure 6.3 B).
During fatigue study, **DASA-BINOL** shows robust switching (10% loss during 5 cycles) in several irradiation cycles. (R)-Binol has also endowed the target molecule with fluorescent properties. By exciting the sample with 330 nm light, an emission maximum at 470 nm was observed (SI Figure 6.6). When the molecule changes from the elongated isomer **O-11** to the cyclopentenone isomer **C-11**, the emission intensity showed a slight decrease from 140 to 120 a.u. By protonated **DASA-BINOL** with various amount of H⁺, the emission band gradually shifted from 470 nm to 400 nm (SI Figure 6.7).

![Figure 6.3](image)

**Figure 6.3** (a) UV-Vis spectrum of **DASA-BINOL** in **DCM** (2×10⁻⁵ M) at 25 °C upon 617 nm light irradiation. (b) Irradiation and thermal isomerization cycles at 25 °C.

### 6.2.3 Switching behavior in LC

The solvent dependent switching behavior of DASA has been discussed in a previous study. However, as far as we know its switching in liquid crystal has never been reported before. We have employed **DASA-BINOL** as a chiral dopant in nematic liquid crystal and its switching behavior was investigated with UV-Vis spectroscopy. The sample was prepared as followed, 1 wt% **DASA-BINOL** was mixed together with E7 at 70 °C. The resulted mixture was filled into a 5 μm thick liquid crystal planar cell at 70 °C by suction. The sample was cooled down to room temperature. During the cooling process, E7 is able to align from an isotropic to nematic phase. It’s worth to mention that we have also tried to mix **DASA-BINOL** in ZLI-1132 liquid crystal mixture, however, it showed poor solubility in this case. Before
measurement, the sample was kept in dark for 1 h to achieve a dark equilibrium. In the initial state, the sample has a strong absorption at $\lambda_{\text{max}} = 640$ nm (purple curve) which is attributed to the blue isomer of DASA-BINOL with extended $\pi$-system (Figure 6.4 A). After irradiation, the absorbance intensity dropped from 0.36 to 0.05, which proves the switching in the liquid crystal material. The back switching is also important since in some cases DASAs show one-way switching in polar protic solvents.\textsuperscript{46,52} To confirm the back switching in the LC, the sample was stored in the dark for 1 h and the absorption peak of DASA switches shown a fully recovery to its original state (Figure 6.4 A, dash lines). For CLCs, DASA-BINOL was used as a photosensitive chiral dopant, to tune the helicity and the phase state of the host LC by the interaction of the host and the guest molecules. The HTP ($\beta$, helical twisting power) value of DASA-BINOL and its changes under red light irradiation were determined by the Grandjean-Cano method.\textsuperscript{54} By measurement, the initial HTP value in cholesteric E7 is $+79 \, \mu m^{-1}$ (Figure 6.4 B) and changed to $+73 \, \mu m^{-1}$ upon in situ irradiation with 617 nm light. The Binol moiety has provided the mixture with intrinsic chirality and induced the helix orientation in the LC phase. When the DASA unit change from triene to cyclopentenone, the conjugation of the push-pull chromophore is eliminated. Due to the change in polarity of the chiral dopant, the interaction between guest and host molecule is weaken and resulting in a lower HTP value.\textsuperscript{1,55} The back switching of the molecule can also be confirmed by the recovery in HTP value from 73 to 78 $\mu m^{-1}$. Furthermore, a mixture of 1 wt % of DASA-BINOL in E7 was capillary-filled into a 5 $\mu m$ thick planar glass cell coated with a polyimide alignment layer. The color of LC cell went from initial green to yellow at PSS\textsubscript{617 nm} (Figure 6.4 C). The newly form state is thermally unstable and can be further thermally switched back at rt. In addition, the color of LC sample changed from light blue to transparent upon red light irradiation (Figure 6.4 A, inserted figure).
Figure 6.4 (a) UV-Vis spectrum of LC cell filled with 1 wt.% DASA-BINOL in E7 before (purple curve) and after (blue curve) light irradiation and its recovery in the dark (dash lines); Color of the LC sample change upon irradiation at 617 nm light (inserted figure). (b) POM images of stripe wedge Grandjean Cano cell filled with 1 wt % DASA-BINOL in E7 before (left) and after (right) light irradiation. (c) POM images of 5 μm-thick planar cell filled with 1 wt % DASA-BINOL in E7 before (left) and after (right) irradiation. The angle between the polarizers is 30°.

6.3 Conclusion

In conclusion, a red light driven switchable chiral dopant containing an (R)-Binol as the chiral moiety and an indoline-DASA as a light responsive unit has been designed. The chiral dopant shown reversible switching with visible light in both solution phase and liquid crystal phase. In CLC system, (R)-Binol has provided the LC phase with certain helicity while isomerization of DASA from a ring open form to a ring closure form is able to tune the helical pitch. The novel red-light responsive chiral switch used as LC dopant as presented here allows the tuning of the wavelength to the red light region in light-responsive liquid crystal devices.

6.4 Experimental section

6.4.1 General remark

All the chemicals were purchased from Sigma-Aldrich and used without any further purification. All organic solvents were analytically pure, and dried or redistilled before using. For column chromatography, silica gel (Silicycles Siliaflash P60, 40–
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60 μm, 230–400 mesh) was used. 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. Wedge cells were purchased from 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 stuck together with the spacing distance of 5 μm fixed by the UV-curing spacer to construct the LC cell.

6.4.2 Measurement of helical twisting power (HTP)

HTP value and its changes upon photoirradiation were determined by the Grandjean Cano method. The definition of HTP is: β=1/(pc), where p is the helical pitch and c is the molar 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=0.00785). The LC mixtures were prepared by doping 1 wt% DASA-BINOL into E7 and then filled it into the wedge cells by capillary force at room temperature. 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 the pitch. HTP changes were achieved by irradiated the resulted sample with a 617 nm LED until no further changes were ever observed.

6.4.3 Characterization

¹H-NMR and ¹³C-NMR spectra were recorded on a Varian AMX-500 (500 MHz), a Varian AMX-400 (400 MHz). Irradiation study ¹H-NMR studies were recorded on a Varian AMX-500 (500 MHz) in dichloromethane-d (CD₂Cl₂). The corresponding chemical shifts were reported in δ values (ppm) relative to deuterochloroform (CDCl₃; ¹H δ=7.25, ¹³C δ=77.2): ¹H δ=5.32, ¹³C δ=54. For ¹H-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 (HRMS) was measured using a double focusing high-resolution mass spectrometer (MS-902, AEI).
Ultraviolet-visible (UV-Vis) spectra were obtained with HP8454 UV-Vis 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 LED lamp (Throlab) at 617 nm. All the optical phenomena of the CLC samples were observed and recorded via polarizing optical microscope (POM, DM2700p, Leica).

**Scheme 6.2 Synthetic route of DASA-BINOL.**

**6.4.4 Synthesis**

(R)-3-Iodo-2,20-methylenedioxy-1,10-binaphthyl (3) Compound 3 was synthesized following the procedure in ref 56. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.49 (s, 1H), 7.94 (dd, $J$ = 8.6, 1.4 Hz, 1H), 7.86 – 7.79 (m, 1H), 7.52 – 7.43 (m, 5H), 7.35 – 7.25 (m, 3H), 5.71 (d, $J$ = 3.4 Hz, 1H), 5.66 (d, $J$ = 3.4 Hz, 1H).

5-Bromoindoline (5) was synthesized following the procedure in ref 57. To a mixture of NaBH$_3$CN (1.89 g, 30.6 mmol) and 5-bromo-1H-indole (2 g, 10.2 mmol), acetic
acid (10 mL) was added at 0 °C. The mixture was stirred for 2 h at rt. The progress of the reaction was monitored by TLC. Acetic acid was removed under vacuum, water (20 mL) was added to the mixture and the pH was adjusted to 8 with an NaOH solution (aq). The solution was extracted with EtOAc (2×30 mL). The combined organic layer was washed with 1 M NaHCO₃ solution (aq) and brine, then dried over Na₂SO₄. The organic solvent was removed under vacuum to yield the crude product as brown solid (1.98 g, 10.2 mmol, quant). The crude product was used for the next step without further purification.

Tert-butyl 5-bromoindoline-1-carboxylate (6) Compound 6 was synthesized following the procedure in ref 58. A mixture of compound 5 (1.2 g, 6 mmol) and di-tert-butyl dicarbonate (1.6 g, 7.3 mmol) in THF (10 mL) was stirred overnight at room temperature and then added into ice water. The obtained solution was extracted with EtOAc (2×30 mL) and washed with brine and dried over Na₂SO₄. After removed the solvent under vacuum, the crude product was purified by chromatography (SiO₂, 100% DCM) to yield compound 6 as an amber solid (1.8 g, 6 mmol, quant). ¹H NMR (400 MHz, CDCl₃) δ 7.70 (s, 1H), 7.25 (d, J = 8.3 Hz, 2H), 3.97 (t, J = 8.7 Hz, 2H), 3.06 (t, J = 8.7 Hz, 2H), 1.52 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 130.2, 116.0, 114.4, 47.7, 28.4, 27.4.

Tert-butyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indoline-1-carboxylate (7) Compound 7 was synthesized following the procedure in ref 59. A mixture of 6 (0.6 g, 2.02 mmol), bis(pinacolato)diboron (0.56 g, 2.22 mmol), potassium acetate (0.59 g, 5.04 mmol) and Pd(dppf)Cl₂ (0.073 g, 0.084 mmol) in dry dioxane (10 mL) was heated at 90 °C overnight. After the reaction mixture was cooled down to room temperature, water (20 mL) was added. The obtained solution was extracted with EtOAc (2×30 mL). The organic layer was washed with brine and dried over Na₂SO₄. The crude product was purified by chromatography (SiO₂, pentane: DCM= 50 : 50) to yield compound 7 as a white solid (0.51 g, 1.48 mmol, 73%). ¹H NMR (400 MHz, CDCl₃) δ 7.82 (s, 1H), 7.63 (d, J = 7.9 Hz, 1H), 7.60 – 7.55 (m, 1H), 3.96 (t, J = 8.6 Hz, 2H), 3.06 (t, J = 8.7 Hz, 2H), 1.55 (s, 9H), 1.33 (d, J = 0.8 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 134.8, 114.0, 83.5, 47.7, 28.4, 24.8.
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\[ \text{[R]-tert-butyl 5-(dinaphtho[2,1-d:1',2'-f][1,3]dioxepin-2-yl)indoline-1-carboxylate (8)} \]

A mixture of 7 (0.1 g, 0.29 mmol), 3 (0.1 g, 0.24 mmol), Pd(PPh\(_3\))\(_4\) (0.01 g, 0.036 mmol) and K\(_2\)CO\(_3\) (0.1 g, 0.72 mmol) in a solvent mixture (toluene 6 mL and EtOH 2 mL) was heated at 90 °C for 2 h. The mixture was degassed before reaction. Solvent was removed under vacuum, the crude product was purified by chromatography (SiO\(_2\), pentane: EtOAc = 97 : 3) to yield compound 8 (0.12 g, 0.23 mmol, 95%) as a white solid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.05 - 7.89 \) (m, 4H), 7.58 (d, \(J = 8.5 \) Hz, 1H), 7.53 - 7.42 (m, 6H), 7.37 - 7.25 (m, 4H), 5.50 (d, \(J = 3.5 \) Hz, 1H), 5.35 (d, \(J = 3.5 \) Hz, 1H), 4.03 (d, \(J = 8.9 \) Hz, 2H), 3.20 - 3.11 (m, 2H), 1.59 (s, 9H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 132.3, 131.7, 131.7, 131.5, 130.3, 128.4, 127.0, 126.7, 126.1, 125.8, 125.3, 125.0, 120.9, 102.5, 28.5. HRMS (ESI) calcd for C\(_{34}\)H\(_{29}\)NO\(_4\) 538.1988 (Na\(^+\)), found 538.1975.

\[ \text{[R]-5-(dinaphtho[2,1-d:1',2'-f][1,3]dioxepin-2-yl)indoline (9)} \]

To compound 8 (0.12 g, 0.23 mmol), trifluoroacetic acid (2 mL) was added and the reaction mixture was stirred overnight at rt. TFA was removed under vacuum. EtOAc (10 mL) was added to the mixture. The solution was washed with a saturated NaHCO\(_3\) solution (aq) and brine, then dried over Na\(_2\)SO\(_4\). The crude product was purified by chromatography (SiO\(_2\), pentane: EtOAc = 50 : 50) to yield compound 9 (0.06 g, 0.14 mmol, 61%) as a yellow solid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.01 - 7.90 \) (m, 4H), 7.60 (d, \(J = 8.6, 1.2 \) Hz, 1H), 7.50 - 7.40 (m, 5H), 7.40 - 7.31 (m, 2H), 6.72 (d, \(J = 8.0 \) Hz, 1H), 5.52 (d, \(J = 3.4 \) Hz, 1H), 5.40 (d, \(J = 3.4 \) Hz, 1H), 3.63 (t, \(J = 8.4 \) Hz, 2H), 3.11 (td, \(J = 8.2, 2.8 \) Hz, 2H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 151.1, 149.0, 132.3, 131.8, 131.7, 131.2, 130.2, 129.9, 129.1, 128.4, 128.3, 127.0, 126.9, 126.7, 126.6, 126.4, 126.0, 125.5, 125.2, 124.9, 120.9, 109.6, 109.4, 102.5, 77.3, 77.0, 76.7, 47.4, 29.7, 22.3. HRMS (ESI) calcd for C\(_{29}\)H\(_{21}\)NO\(_2\) 416.16451 (H\(^+\)), found 416.1643.

5-(furan-2-ylmethylene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (10)

Compound 10 was synthesized following the procedure in ref 60. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.60 \) (d, \(J = 3.8 \) Hz, 1H), 8.39 (s, 1H), 7.83 (d, \(J = 1.6 \) Hz, 1H), 6.71 (ddd, \(J = 3.9, 1.7, 0.8 \) Hz, 1H), 3.37 (d, \(J = 3.0 \) Hz, 6H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 162.4, 160.8, 151.3, 151.1, 150.4, 140.9, 128.0, 115.1, 111.4, 39.4, 28.9, 28.2.
[R]-5-((2Z,4E)-5-(5-(dinaphtho[2,1-d:1',2'-f][1,3]dioxepin-2-yl)indolin-1-yl)-2-hydroxypenta-2,4-dien-1-ylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (11) A mixture of compound 9 (0.06 g, 0.14 mmol) and compound 8 (0.033 g, 0.14 mmol) in DCM (2 ml) was stirred at room temperature for 72 h. The reaction mixture was purified by chromatography (SiO₂, pentane: DCM = 50 : 50 ~ DCM : MeOH = 99 : 1) to yield compound 11 (0.036 g, 0.06 mmol, 40%) as a blue solid.

^1^H NMR (400 MHz, CD₂Cl₂) δ 12.44 (s, 1H, OH), 8.00 (ddd, J = 19.9, 9.3, 5.3 Hz, 6H, Binol), 7.74 (d, J = 6.0 Hz, 1H, vinylH), 7.66 – 7.58 (m, 1H, VinylH), 7.57 – 7.41 (m, 7H, Binol), 7.40 – 7.24 (m, 4H, Binol, ArH), 7.20 (d, J = 8.7 Hz, 1H, Binol), 6.79 (d, J = 12.6 Hz, 1H, VinylH), 6.52 (t, J = 8.4 Hz, 1H, ArH), 6.44 (dd, J = 6.0, 2.1 Hz, 1H, VinylH), 6.24 (d, J = 18.6 Hz, 1H, VinylH), 5.59 – 5.51 (m, 1H, OCH₂O), 5.43 (t, J = 3.0 Hz, 1H, OCH₂O), 5.35 – 5.29 (m, 1H, VinylH), 4.17 (t, J = 8.1 Hz, 1H, VinylH), 4.12 (s, 1H, VinylH), 3.87 – 3.71 (m, 1H, NCH₂CH₂Ar), 3.59 (m, J = 8.7, 2.8 Hz, 1H, NCH₂CH₂Ar), 3.47 – 3.26 (m, 6H, NCH₂CH₂Ar, NCH₃), 3.18 – 3.06 (m, 4H, NCH₂CH₂Ar, NCH₃).

^1^H NMR (400 MHz, CD₃OD) δ 8.11 – 7.91 (m, 4H), 7.75 (dd, J = 6.0, 2.0 Hz, 1H), 7.44 (td, J = 8.1, 7.7, 5.0 Hz, 4H), 7.49 – 7.18 (m, 6H), 6.58 (dd, J = 8.2, 1.9 Hz, 1H), 6.40 (dd, J = 6.0, 2.0 Hz, 1H), 5.48 (t, J = 3.4 Hz, 1H), 5.33 (t, J = 3.5 Hz, 1H), 5.30 – 5.25 (m, 1H), 4.03 (d, J = 3.5 Hz, 1H), 3.81 – 3.62 (m, 1H), 3.41 (d, J = 8.8 Hz, 1H), 3.23 (d, J = 8.1 Hz, 6H), 3.03 (d, J = 8.7 Hz, 2H).

^1^C NMR (101 MHz, CD₂Cl₂) δ 162.7, 151.1, 150.2, 134.5, 132.2, 132.1, 131.8, 131.7, 131.6, 131.1, 130.4, 130.2, 130.1, 129.9, 129.8, 129.7, 128.9, 128.9, 128.4, 128.3, 127.3, 126.8, 126.7, 126.6, 126.5, 126.4, 126.4, 126.2, 126.0, 125.6, 125.5, 125.2, 124.9, 120.9, 105.6, 105.5, 102.7, 60.2, 47.6, 47.4, 47.1, 28.7, 28.5, 28.3, 28.2, 28.1.

HRMS (ESI) calcd for C₄₀H₃₁N₅O₆ 650.22856 (H+), found 650.2281.
Figure 6.5 In situ kinetic plot of the switching cycle of DASA-BINOL in DCM (2×10^{-5} M), monitored at \( \lambda_{\text{max}} = 626 \text{ nm} \) and 298 K.

Figure 6.6 PL spectrum of DASA-BINOL in DCM (2×10^{-5} M) before (red curve) and after (blue curve) 617 nm light irradiation.
Figure 6.7 (a) DASA-BINOL in DCM with various amount of TFA. (b) PL spectrum of DASA-BINOL in DCM (2×10^-5 M) with various amount of TFA.

Figure 6.8 1H-NMR spectrum of DASA-BINOL in CD2Cl2 before (blue) and after (red) irradiation.
Figure 6.9 $^1$H-NMR spectrum of DASA-BINOL in CD$_2$Cl$_2$.

Figure 6.10 $^1$H-NMR spectrum of DASA-BINOL in CD$_3$OD.

Figure 6.11 Cosy $^1$H-$^1$H-NMR spectrum of DASA-BINOL in CD$_2$Cl$_2$.
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Figure 6.12 Cosy $^1$H-$^1$H-NMR spectrum of DASA-BINOL in CD$_3$OD

Figure 6.13 HSQC $^1$H-$^{13}$C NMR spectrum of DASA-BINOL in CD$_2$Cl$_2$

Figure 6.14 Circular Dichroism spectrum of DASA-BINOL in DCM $10^{-4}$ M at rt before (dash line) and after (black curve) 617 nm light irradiation. The CD signals show no difference before and after irradiation.
6.5 Reference

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