Supporting Information

Light-induced Wide Range Color Switching of Liquid Crystal Blue Phase doped with Hydrogen-bonded Chiral Azobenzene Switches

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1. Synthesis and characterization of BNAzo

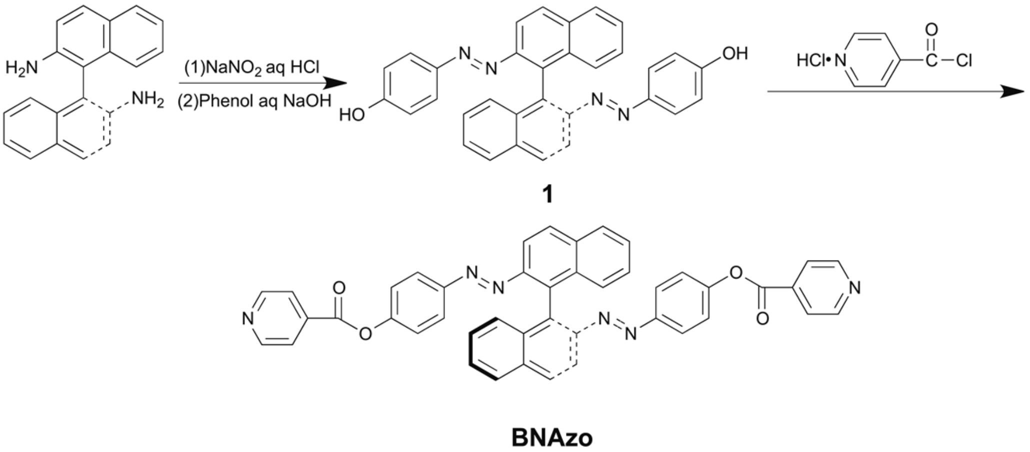

Fig. S1 Synthetic routes to the proton acceptor of H-bonded CAS

i Compound 1

4,4'- ((S)-[1,1'-binaphthalene]-2,2'-diyl)bis(diazene-2,1-diyl))diphenol:

Aqueous $NaNO_2$ (0.58 g, 8.44 mmol) was cautiously poured into a stirred solution of (S)-(-)-1,1'-Binaphthyl-2,2'-diamine (1.00g, 3.52mmol) in hydrochloric acid (4.8 mmol/ml, 17 ml) by keeping the temperature below 3 °C. After 30 min, ice-cooled aqueous solution (15 ml) of phenol (0.73g, 7.74mmol) and NaOH (0.90g, 22.60mmol) was slowly poured into the mixture (0-5 °C). The reaction mixture was stirred for 7h and neutralized to PH=7. The orange suspension was washed with water, and red solid was obtained after being dried and purified by column chromatography, Yield, 53%.

^{1}H NMR (400MHz, DMSO): δ= 10.18 (s, 2H, Ar-OH), 8.18 (d, J=8.9Hz, 2H, Ar-H), 8.10 (m, 4H, Ar-H), 7.57 (t, J=7.5Hz, 2H, Ar-H), 7.35 (t, J=8.1Hz, 2H, Ar-H), 7.28 (d, J=8.35Hz, 2H, Ar-H), 7.18 (d, J=8.73Hz, 4H, Ar-H), 6.70 (d, J=8.73Hz, 4H, Ar-H).

ii **BNAzo ((S)-[1,1'-binaphthalene]-2,2'-diyl)bis(diazene-2,1-diyl))diphenol isonicotinate (H-bonded proton acceptor):**

To a stirred suspension of isonicotinoyl chloride hydrochloride (0.07 g, 0.4 mmol) in THF (10 ml), triethylamine (0.45 ml) was added slowly. A solution of compound 1 (0.1 g, 0.2 mmol) dissolved in THF (5 ml) was added dropwise into the above suspension. The mixture was continuously stirred at room temperature for 72 h, filtered and concentrated in vacuum. The precipitate was washed with distilled water several times and then filtered and purified by column chromatography to obtain red solid, Yield, 50%.

^{1}H NMR (400MHz, Acetone): δ= 8.88 (d, J=4.56Hz, 4H, N-H), 8.18 (d,J=9.2Hz, 2H, Ar-H), 8.11 (d, J=7.92Hz, 2H, Ar-H), 8.02 (t, J=4.68Hz, 4H, N-H), 7.57 (t, J=7.4Hz, 2H, Ar-H), 7.50 (d, J=8.36Hz, 2H, Ar-H), 7.42 (d, J=8.8Hz, 4H, Ar-H), 7.35 (m, 4H, Ar-H), 7.14 (d, J=8.76Hz, 4H, Ar-H).

IR (thin film) ν_{max}: 2969, 1744, 1596, 1489, 1408, 1263, 1220, 1061 and 749cm^{-1}.

^{13}C NMR ($CDCl_3$) δ=163.27, 151.88,150.83, 150.49, 148.20, 137.68, 136.85, 134.59, 134.18, 130.91, 129.28, 128.84, 128.17, 127.89, 127.53, 126.89, 124.11, 123.32, 121.76, 114.15, 77.33, 77.01, 76.69, 65.57, 30.58, 19.19, 13.73.

2. Preparation of H-bonded CAS

The H-bonded chiral azobenzene switches (BNAzo-MHA and BNAzo-OCA) are prepared by mixing the proton acceptor (BNAzo) with two proton donors (MHA, OCA) in molar ratio of 1:2 in THF respectively, followed by slow evaporation.

3. Materials and instruments

In this study, SLC1717 (isotropic temperature, T_i=92 °C; 20 °C，589 nm, Δn=0.201, Slichem Liquid Crystal Material Co., Ltd.) S811 (Beijing Lyra Tech), Methylhexanoic acid (MHA, Alfa Aesar) and octanoic acid (OCA, Alfa Aesar) were used. In order to induce BPs, H-bonded bent-shape dopant (TBOA-MBIN) and S811 were introduced into LCs system as shown in Fig. S2. TBOA-MBIN was synthesized according to the procedure in our previous work.[1] The FT-IR spectra were recorded on a Nicolet 5700 spectrometer at frequencies ranging from 400-4000 cm^{-1}. The samples were observed by POM (Leica DM2500P) with a hot stage calibrated with an accuracy of ± 0.1 °C (Linkam, THBS-600). The reflection spectra were examined with AvaSpec-2048 spectrophotometer in reflection mode. UV/Vis and CD spectrum were taken by a JASCO J810 spectrometer and a JASCO V550 spectrometer, respectively.

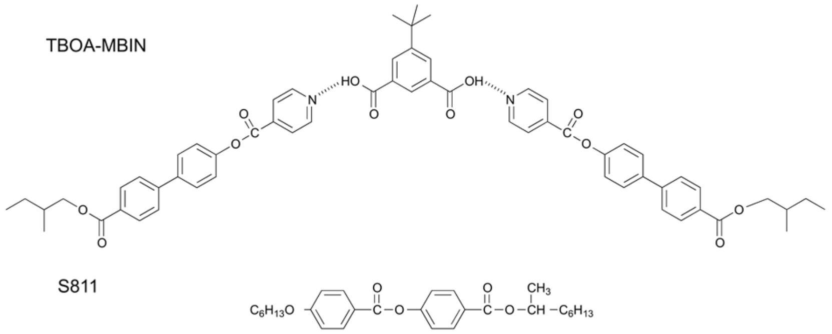

Fig. S2 The chemical structures of TBOA-MBIN and S811

4. Characterization of H-bonded molecular switches

We used FT-IR spectrometry to distinguish the existence and intensity of H-bonding in this work. Fig. 2 shows the FT-IR spectra of the H-bonded CAS and their precursors. The FT-IR spectra confirm the presence of H-bonding obtained by self-assembly process. As is shown in Fig. 2a, two peaks around 2500 and 1900 cm^{-1} indicate the presence of hydrogen bonds, which almost coincides with the position of –OH stretching of H-bond between the carboxylic acid and pyridyl group. Similarly, such phenomenon can also be observed in BNAzo-OCA as shown in Fig. 2b indicating that two groups of H-bonded CAS (BNAzo-MHA and BNAzo-OCA) were successfully assembled. [2]

In Fig. S3, the thermal stability of the H-bonded CAS was studied by the variable-temperature FT-IR spectroscopy. With the temperature increasing, the peaks indicating the H-bonds between the -OH and pyridyl group (around 2500 and 1900 cm-1) became weaker (as the inset shows), which means the elevation of temperature affected interaction between proton donors and acceptors. We can also find that the H-bonded CAS (BNAzo-MHA, BNAzo-OCA) have good thermal stability across a temperature range of 30 °C to 110 °C, which sufficiently satisfy our experimental condition.

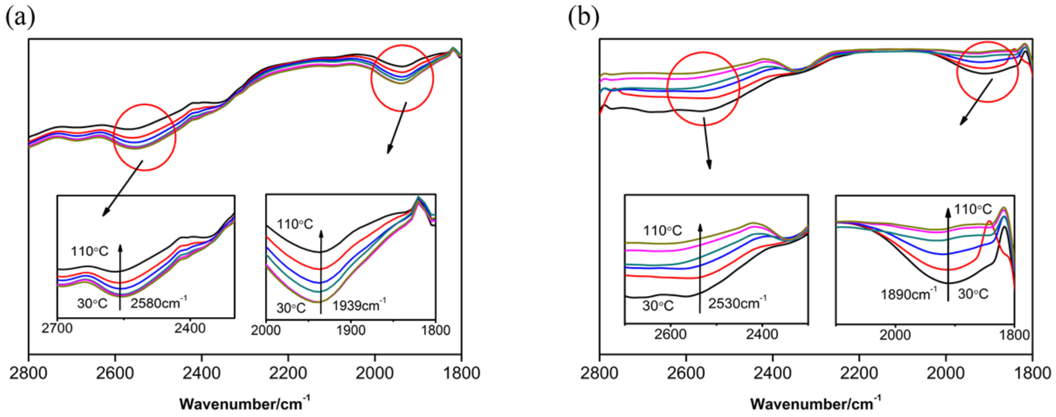

Fig. S3 Variable-temperature FT-IR spectra of H-bonded CAS (a): BNAzo-MHA; (b): BNAzo-OCA.

5. Circular dichroism spectroscopy and UV/Vis spectrosopy

Fig. 3 shows the change in UV and CD spectra of BNAzo-MHA (a), BNAzo-OCA (b), under various UV irradiation condition. Studies shows that the *trans* form of the azobenzene in BNAzo exhibited absorption maxima at 340 nm due to a π-π* transition and at 400 nm due to an n-π* transition. It is found that after photoirradiation at 365 nm (2 mW·cm^{-2}), there is a decrease in the π-π* band and a relatively small amount of increase in the n-π* band, which indicates that *trans-cis* photoisomerization of BNAzo takes place on photoirradiation. Meanwhile, CD spectra exhibit distinct bands for n-π* and π-π* transitions of the azochromophore. For example, at initial state, BNAzo-MHA shows a negative band and positive band for the π-π* transitions at 320 nm and 400 nm respectively followed by a relatively weak negative band at 450 nm, upon UV irradiation, with the influence of isomerization of azobenzene moieties, we can find a gradual decrease at 450 nm due to the formation of *cis* isomer, and the pattern of CD Cotton effect between 300 and 400 nm become weak due to the π-π* transitions, which is corresponding to the phenomenon we observed in UV-Vis spectra.[3]

Moreover, to prove the photoisomerization of azobenzene has no impact on the thermoresponsive behavior in this work, we measured the change in absorption of H-bonded CAS in 1,4-dioxane at various temperatures. Fig. S4 shows nearly no change is found in the absorption spectra, which indicates that isomerization of azobenzene structure does not take place during heat treatment process, therefore, the light and temperature induced processes of H-bonded CAS are two separative processes.

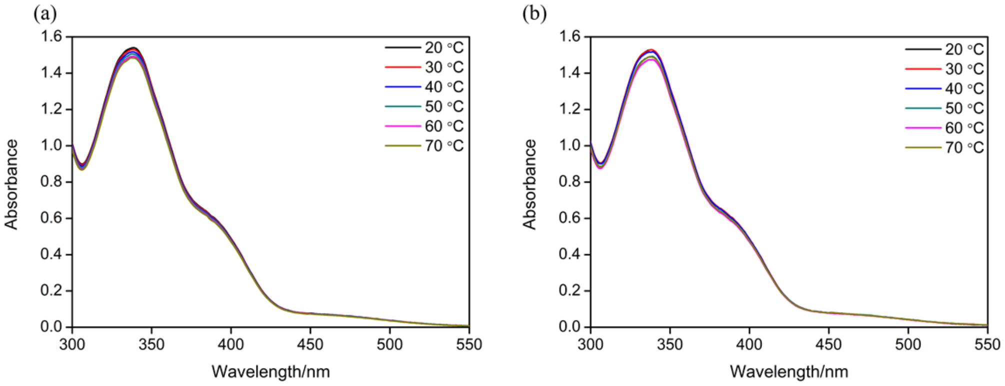

Fig. S4 UV/Vis absorption spectra of H-bonded CAS at various temperatures (a): BNAzo-MHA; (b): BNAzo-OCA

6. Measurement of pitch length by Cano wedge method

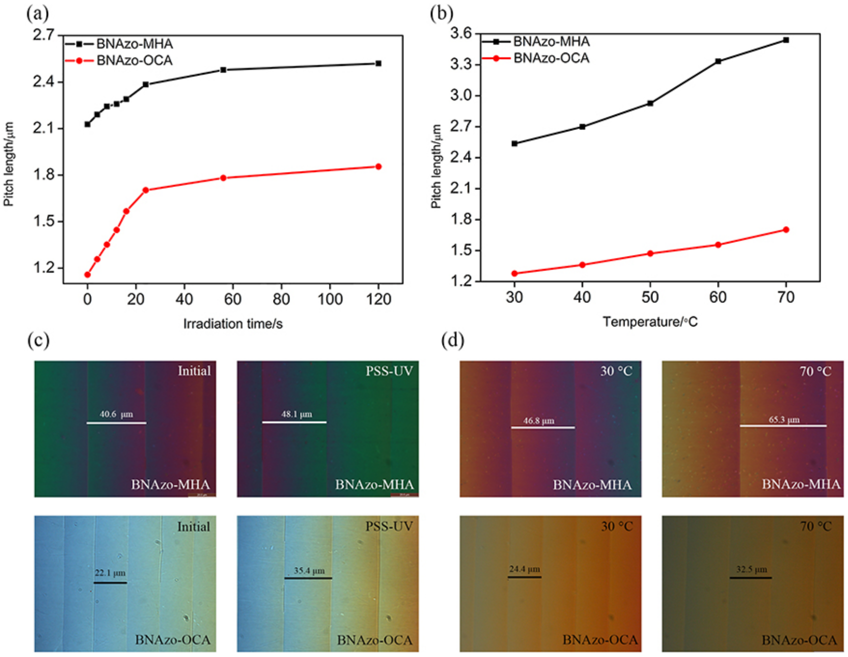

Fig S5. Changes in the helical pitch of 1.0 wt% chiral dopants in SLC1717 (a) upon UV irradiation; (b) at various temperatures and POM micrographs of Cano wedge cells (c) upon UV irradiation; (d) at various temperatures.

We studied photo and thermoresponsive behavior of H-bonded CAS in the commercially available N-LCs host (SLC1717) by using the Grandjean-Cano method. The HTP value was used to characterize the ability of chiral dopants for twisting Cholesteric mesophase which is defined as the value of β and expressed by following equation: β=1/Pc, where P is the helical pitch and c is the concentration of the chiral dopants. Two LCs samples were prepared by mixing the H-bonded CAS with SLC1717 in CH_2Cl_2, followed by the removal of solvent, the weight ratios of which are corresponding to chiral dopant (BNAzo-MHA, BNAzo-OCA) : SLC1717 host =1:99 respectively. Then we put the mixtures into wedges cell, which had been coated with polyimide and rubbed to align LC moieties. Owing to the twisting ability of chiral dopants, the N-LCs host is induced to exhibit helical structure so we can see Cano lines by using POM. By using the Cano wedge method, the pitch length can be determined according to the equation: $p= 2R\tan\theta$, where R represents the distance between the Cano lines and θ is the wedge angle ($\theta=1.5$ °, $\tan\theta=0.0262$). Then the HTP value of chiral dopants can be calculated according to the equation we mentioned above. Therefore, both helical pitch and HTP can be obtained through Cano wedge method.

Moreover, the photo and thermoresponsive process are reversible under 450 nm light irradiation (10 mW/cm^{2}) and during cooling process respectively. As Fig. S5(c) and Fig. S5(d) shows, the distance between Cano lines increased under UV irradiation (365 nm, 6 mW/cm^{2}) as well as with increasing temperature. Furthermore, as shown in Table S1, the change of HTP of BNAzo-OCA (37.6%) is bigger than that of BNAzo-MHA (15.6%) upon UV irradiation and the initial HTP of BNAzo-OCA is also the biggest, which coincide with the aspect ratio we listed in Fig. 1.

Table S1. Helical twisting power (in SLC1717) at initial state and photo stationary state upon UV irradiation (365nm, 6 mW·cm^{-2}) and at different temperatures (30 °C and 70 °C)

H-bonded Chiral Molecular Switches	HTP（wt%）/μm^{-1}		ΔHTP[a] (μm^{-1})	Change in HTP[b]（%）
	Initial	PSS$_{UV}$		
BNAzo-MHA	47.0	39.7	7.3	15.6
BNAzo-OCA	86.4	53.9	32.5	37.6
	HTP（wt%）/μm^{-1}		ΔHTP[a] (μm^{-1})	Change in HTP[b]（%）
	30°C	70°C		
BNAzo-MHA	39.4	28.3	11.1	28.1
BNAzo-OCA	78.2	58.7	19.5	25.3

[a] ΔHTP is calculated by subtracting the photostationary HTP from the initial HTP value.

[b] The change in HTP is calculated by dividing ΔHTP by initial HTP.

7. Bragg reflection wavelength of BPs samples

We measured the reflection band of A0-A4 at initial BP I temperature. As shown in Fig. S6, the reflection spectra clearly show that the samples A0-A4 exhibited reflection band at around 525 nm, which means the initial lattice constant of DTA are almost the same in samples A0-A4 at each initial BP I temperature.

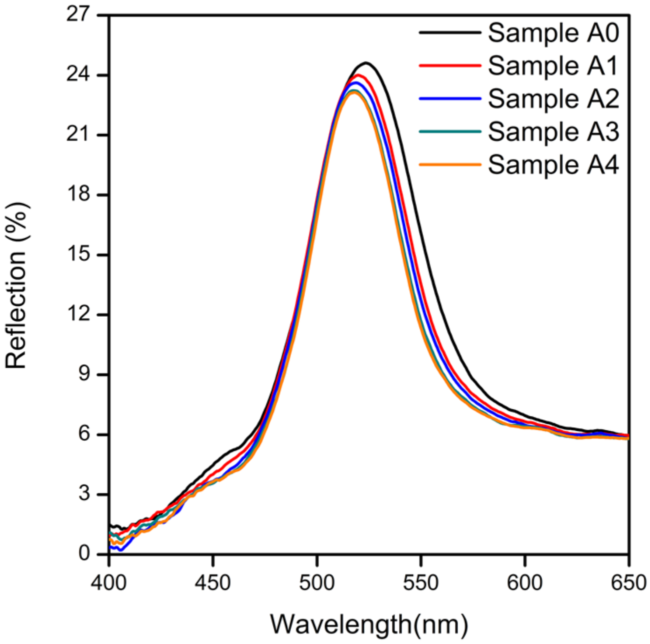

Fig.S6 Reflection wavelength of five samples (A0, A1, A2, A3 and A4) at initial BP state

References for Supporting Information

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2. T. Kato, J. M. Frechet, P. G. Wilson, T. Saito, T. Uryu, A. Fujishima, C. Jin and F. Kaneuchi, *Chem. Mater.*, 1993, **5**, 1094-1100.

3. H. Goto and K. Kawabata, *Polym. Chem.*, 2011, **2**, 1098-1106.