

Supporting Information for:

Light-controllable Reflection Wavelength of Blue Phase liquid Crystallines doped with Azobenzene-Dimers

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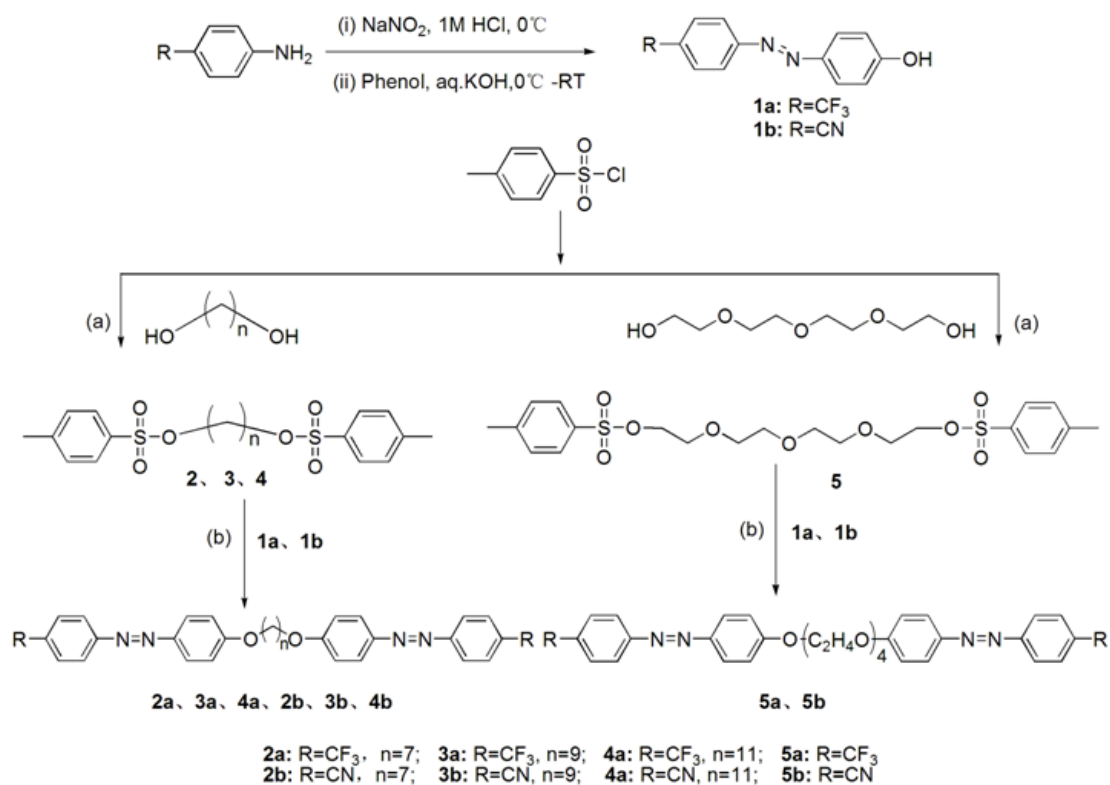
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1. Synthesis and properties

1.1 General procedures for the synthesis of azobenzene-dimers: 2a, 2b, 3a, 3b, 4a, 4b, 5a, 5b.



Scheme S1 synthetic route to the target compounds. Reagents and conditions: (a) Et₃N, (CH₃)₃N·HCl, CH₂Cl₂, RT; (b) K₂CO₃, DMF, 90 °C, reflux

The azobenzene-dimers were synthesized following the general procedure as shown in Scheme S1^[1, 2]. The structure of the compounds was confirmed by ¹H NMR, FT-IR and MALDI-TOF MS analysis.

4-((4-(trifluoromethyl) phenyl) diazenyl) phenol (**1a**)

4-(trifluoromethyl)benzenamine (11.2 g, 0.07 mol) was added to stirred solution of hydrochloric acid in 100ml water at 0-5 °C for 30 min. Then dropping another solution mixed with NaNO₂ (5.1 g, 0.075 mol) and urea (6 g) in 20 ml water to the reaction solution and stirred 30min. After that, a solution mixed with phenol (6.6 g, 0.07 mol) and KOH (7.5 g, 0.08 mol) in 100 ml water was dropping into the reaction solution and stirred 30min. The whole process was kept in ice bath. At last, adjust the

PH of the mixture with hydrochloric acid and KOH to 3-5 and filtered, the solid was washed by water and removed the water in vacuum to get a brown solid. Yield 86%, 16 g. FT-IR (KBr, cm^{-1}): 3270, 1590, 1503, 1327, 1248, 1140, 1121, 1065, 850.

4-((4-hydroxyphenyl)diazanyl)benzonitrile (1b)

The same procedure as described for compound **1a** using 4-aminobenzonitrile (8.4 g, 0.07 mol) replaced the 4-(trifluoromethyl)benzenamine and got a yellow solid. Yield 82.5%, 13.1 g. FT-IR (KBr, cm^{-1}): 3318, 2239, 1606, 1586, 1462, 1280, 1217, 1138, 845, 556.

1, 7-bis (4-methylbenzenesulfonate) heptane (2)

4-methylbenzene-1-sulfonyl chloride (9 g, 45 mmol) in CH_2Cl_2 (50 mL) was added to a stirred solution of heptane-1, 7-diol (2 g, 15 mmol), Et_3N (6 g, 60 mmol), and $\text{Me}_3\text{N}\cdot\text{HCl}$ (0.3 g, 3 mmol) in CH_2Cl_2 (100 mL) at room temperature. The reaction was allowed to proceed for 1 h. The reaction mixture was filtrated to remove insoluble salts. Next, the mother liquor was evaporated and the residue was dissolved in methanol, filtrated, and precipitated in excess diethyl ether. The dissolution/precipitation cycle was repeated once. The macroinitiator was isolated by filtration and dried in vacuo got a white solid. Yield 88%, 5.8 g. FT-IR (KBr, cm^{-1}): 2977, 2926, 2859, 1598, 1353, 1189, 1172, 955, 839, 816, 666, 574, 555, 529.

1, 9-bis (4-methylbenzenesulfonate) nonane (3)

The same procedure as described for compound **2** using nonane-1, 9-diol (2.4 g, 15 mmol) replaced the heptane-1, 7-diol and got a white solid. Yield 85%, 6 g. FT-IR (KBr, cm^{-1}): 2971, 2925, 2857, 1598, 1475, 1353, 1189, 1172, 954, 839, 816, 666, 574, 556, 532.

1, 11-bis (4-methylbenzenesulfonate) undecane (4)

The same procedure as described for compound **2** using undecane-1, 11-diol (2.8 g, 15 mmol) replaced the heptane-1, 7-diol and got a white solid. Yield 79%, 5.9 g. FT-IR (KBr, cm^{-1}): 2967, 2925, 2853, 1597, 1474, 1353, 1188, 1172, 1098, 952, 839, 816, 667, 575, 556, 534.

2,2'-(2,2'-oxybis(ethane-2,1-diyl)bis(oxy))bis(ethane-2,1-diyl)

dis(4-methylbenzenesulfonate) (5)

4-methylbenzene-1-sulfonyl chloride (9 g, 45 mmol) in CH₂Cl₂ (50 mL) was added to a stirred solution of tetraethylene glycol (2.9 g, 15 mmol), Et₃N (6 g, 60 mmol), and Me₃N·HCl (0.3 g, 3 mmol) in CH₂Cl₂ (100 mL) at room temperature. The reaction was allowed to proceed for 1 h. The reaction mixture was filtrated to remove insoluble salts. Next, the mother liquor was evaporated and the residue was purified by silica-gel column chromatography with CH₂Cl₂ and got a pale yellow liquid. Yield 76%, 6.2 g. FT-IR (KBr, cm⁻¹): 2950, 2876, 1598, 1454, 1355, 1190, 1176, 1097, 1018, 922, 817, 776, 664, 582, 554.

1, 7-bis (4-((4-(trifluoromethyl) phenyl) diazenyl)phenoxy)heptane (2a)

1a (2.4 g, 9 mmol) and **2** (1.8 g, 4 mmol) were dissolved in solvent of 50 ml DMF, and then added K₂CO₃ (1.2 g, 8.7 mmol). The mixture was stirred at 90 °C for 20h. After that, the mixture was cooled to room temperature and poured into 300 ml water and filtered. The solid was washed by water and dried in vacuo. At last, it was purified by recrystallization with THF twice and got yellow solid. Yield 71%, 1.8 g. ¹H-NMR (400 MHz, CDCl₃, TMS) δH/ppm: 7.95 (m, 8H), 7.75 (d, J= 8.4 Hz, 4H), 7.02 (d, J=8.8 Hz, 4H), 4.07 (t, J=12.8 Hz, 4H), 1.86 (m, 4H), 1.54 (m, 6H). FT-IR (KBr, cm⁻¹): 2939, 2866(-CH₂-), 1603(-N=N-), 1582, 1499, 1317(-CF₃), 1247(-O-), 1137, 1062, 851. MALDI-TOF MS (M+H) calcd for C₃₃H₃₀F₆N₄O₂: 628.2, found: 628.2.

1, 7-bis (4-((4-cyanphenyl) diazenyl)phenoxy)heptane (2b)

1b (2 g, 9 mmol) and **2** (1.8 g, 4 mmol) were dissolved in solvent of 50 ml DMF, and then added K₂CO₃ (1.2 g, 8.7 mmol). The mixture was stirred at 90 °C for 20 h. After that, the mixture was cooled to room temperature and poured into 300 ml water and filtered. The solid was washed by water and dried in vacuum. At last, it was purified by recrystallization with THF twice and got yellow solid. Yield 6.9%, 1.5 g. ¹H-NMR (400 MHz, CDCl₃, TMS) δH/ppm: 7.94 (m, 8H), 7.79 (d, J=8.4 Hz, 4H),

7.02 (d, J=9.2 Hz, 4H), 4.08 (t, J=12.8 Hz, 4H), 1.86 (m, 4H), 1.52 (m, 6H). FT-IR (KBr, cm^{-1}): 2938, 2861(-CH₂-), 2226(-CN), 1603(-N=N-), 1581, 1499, 1255(-O-), 1141, 847, 559. MALDI-TOF MS (M+H) calcd for C₃₃H₃₀N₆O₂: 542.2, found: 542.2.

1, 9-bis (4-((4-(trifluoromethyl) phenyl) diazenyl)phenoxy)nonane (3a)

The same procedure as described for compound **2a** using **3** (1.9 g, 4 mmol) replaced the **2** and got a yellow solid. Yield 71%, 1.9 g. ¹H-NMR (400 MHz, CDCl₃, TMS) δ H/ppm: 7.94 (m, 8H), 7.75 (d, J=8.4 Hz, 4H), 7.02 (d, J=8.8 Hz, 4H), 4.06 (t, J=12.8 Hz, 4H), 1.83 (m, 4H), 1.50 (m, 4H), 1.40 (m, 6H). FT-IR (KBr, cm^{-1}): 2943, 2870(-CH₂-), 1603(-N=N-), 1582, 1501, 1317(-CF₃), 1256(-O-), 1140, 1062, 851. MALDI-TOF MS (M+H) calcd for C₃₅H₃₄F₆N₄O₂: 656.3, found: 656.2.

1, 9-bis (4-((4-cyanophenyl) diazenyl) phenoxy)nonane (3b)

The same procedure as described for compound **3a** using **1b** (2 g, 9 mmol) replaced the **1a** and got a yellow solid. Yield 69%, 1.6 g. ¹H-NMR (400 MHz, CDCl₃, TMS) δ H/ppm: 7.94 (m, 8H), 7.79 (d, J=8.0 Hz, 4H), 7.02 (d, J=8.8 Hz, 4H), 4.06 (t, J=12.8 Hz, 4H), 1.84 (m, 4H), 1.49 (m, 4H), 1.42 (m, 6H). FT-IR (KBr, cm^{-1}): 2932, 2845(-CH₂-), 2233(-CN), 1600(-N=N-), 1581, 1495, 1466, 1248(-O-), 1140, 857, 566. MALDI-TOF MS (M+H) calcd for C₃₅H₃₄N₆O₂: 570.3, found: 570.3.

1, 11-bis (4-((4-(trifluoromethyl) phenyl) diazenyl)phenoxy)undecane (4a)

The same procedure as described for compound **2a** using **4** (2 g, 4 mmol) replaced the **2** and got a yellow solid. Yield 49%, 1.4 g. ¹H-NMR (400 MHz, CDCl₃, TMS) δ H/ppm: 7.94 (m, 8H), 7.79 (d, J=8.8 Hz, 4H), 7.01 (d, J=8.8 Hz, 4H), 4.05 (t, J=12.8 Hz, 4H), 1.83 (m, 4H), 1.49 (m, 4H), 1.33 (m, 10H). FT-IR (KBr, cm^{-1}): 2938, 2851(-CH₂-), 1602(-N=N-), 1581, 1500, 1318(-CF₃), 1254(-O-), 1139, 1063, 854. MALDI-TOF MS (M+H) calcd for C₃₇H₃₈F₆N₄O₂: 684.3, found: 684.2.

1, 11-bis (4-((4-cyanophenyl) diazenyl)phenoxy)undecane (4b)

The same procedure as described for compound **4a** using **1b** (2 g, 9 mmol) replaced the **1a** and got a yellow solid. Yield 56%, 1.3 g. ¹H-NMR (300 MHz, CDCl₃, TMS)

δ H/ppm: 7.96 (m, 8H), 7.76 (d, J=8.4 Hz, 4H), 7.03 (d, J=9.0 Hz, 4H), 4.07 (t, J=13 Hz, 4H), 1.85 (m, 4H), 1.49 (m, 4H), 1.36 (m, 10H). FT-IR (KBr, cm^{-1}): 2932, 2846(-CH₂-), 2233(-CN), 1600(-N=N-), 1581, 1495, 1466, 1245(-O-), 1138, 857, 565. MALDI-TOF MS (M+H) calcd for C₃₇H₃₈N₆O₂: 598.3, found: 598.3.

2,2'-(4,4'-(2,2'-(2,2'-oxybis(ethane-2,1-diyl)bis(oxy))bis(ethane-2,1-diyl))bis(oxy)bis(4,1-phenylene))bis(1-(4-(trifluoromethyl)phenyl)diazene) (5a)

The same procedure as described for compound 2 using 5 (2.2g, 4mmol) replaced the heptane-1, 7-diol and got a yellow solid. Yield 68%, 1.9 g. ¹H-NMR (400 MHz, CDCl₃, TMS) δ H/ppm: 7.92 (m, 8H), 7.74 (d, J=8.4 Hz, 4H), 7.03 (d, J=9.2 Hz, 4H), 4.22 (t, J=9.6 Hz, 4H), 3.91 (t, J=9.6 Hz, 4H), 3.74 (m, 8H). FT-IR (KBr, cm^{-1}): 2929, 2884(-CH₂-), 1598(-N=N-), 1503, 1325(-CF₃), 1255(-O-), 1130, 1108, 1063, 854. MALDI-TOF MS (M+H) calcd for C₃₄H₃₂F₆N₄O₅: 690.2, found: 690.2.

4,4'-(4,4'-(2,2'-(2,2'-oxybis(ethane-2,1-diyl)bis(oxy))bis(ethane-2,1-diyl))bis(oxy)bis(4,1-phenylene))bis(diazene-2,1-diyl)dibenzonitrile (5b)

The same procedure as described for compound 5a using 1b (2 g, 15 mmol) replaced the 1a and got a yellow solid. Yield 65%, 1.6 g. ¹H-NMR (600 MHz, CDCl₃, TMS) δ H/ppm: 7.91 (m, 8H), 7.78 (d, J=8.4 Hz, 4H), 7.03 (d, J=9.6 Hz, 4H), 4.22 (t, J=9.6 Hz, 4H), 3.90 (t, J=9 Hz, 4H), 3.74 (m, 8H). FT-IR (KBr, cm^{-1}): 2941, 2883(-CH₂-), 2225(-CN), 1600(-N=N-), 1584, 1500, 1256(-O-), 1139, 1105, 850, 561. MALDI-TOF MS (M+H) calcd for C₃₄H₃₂N₆O₅: 604.2, found: 604.0.

2. The DSC and POM picture of azobenzen-dimers

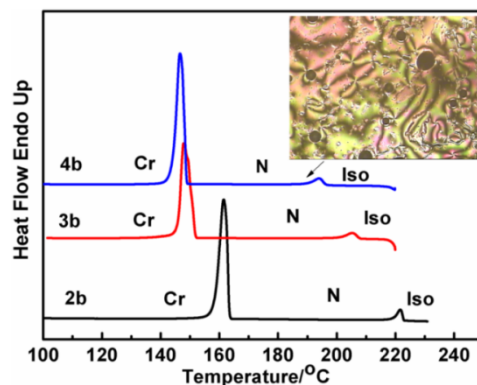


Fig. S1 The DSC measurements of compounds **2b-4b** on cooling recycles and the POM texture of compound **4b** at 193 °C

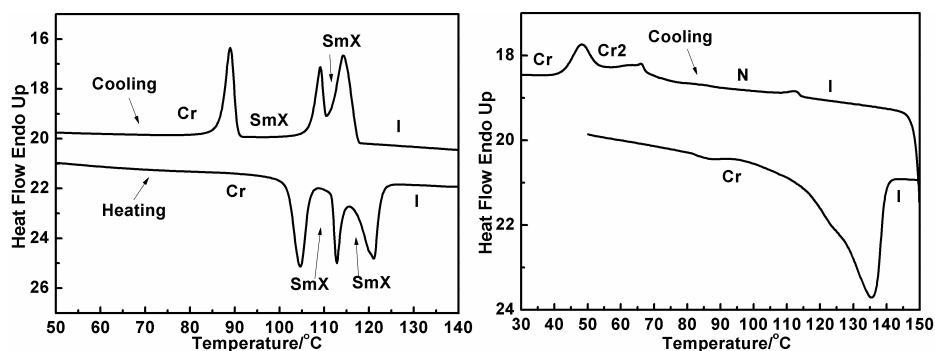


Fig. S2 The DSC measurement of compounds **5a** (left) and **5b** (right) on heating and cooling recycle

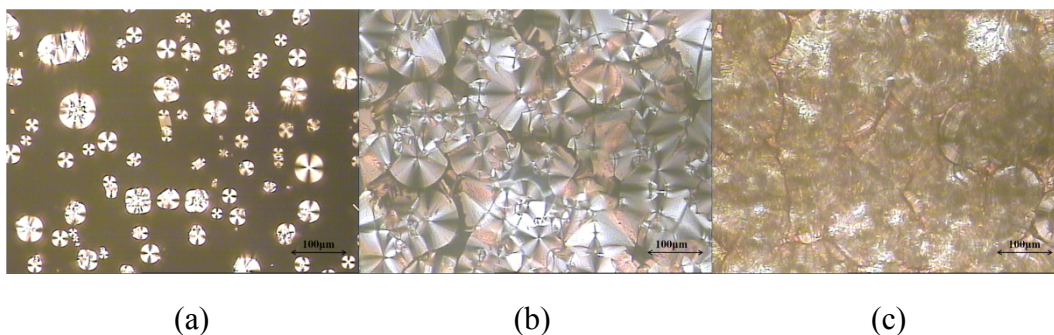


Fig. S3 The POM pictures of **5a**: (a) the fan texture at 114 °C; (b) the fan texture at 110 °C; (c) the crystalline at 80 °C.

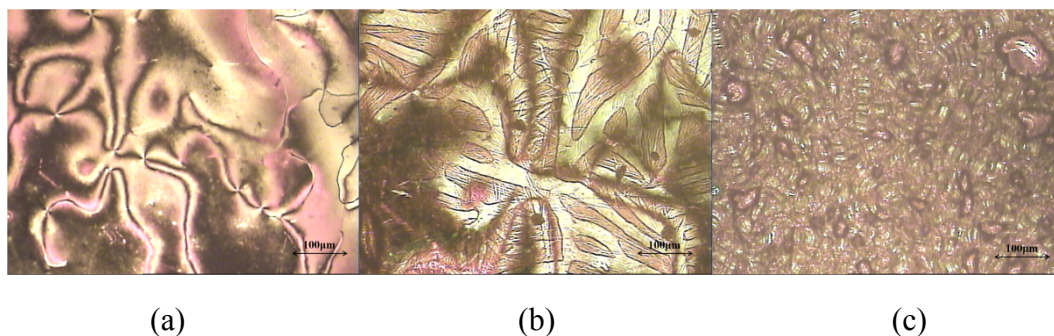


Fig. S4 the POM picture of **5b**: (a) the schlieren texture at 100 °C; (b) the crystalline state at 60 °C; (c) the crystalline at 30 °C.

The initial phase sequences and corresponding transition temperatures of the compounds were determined by the polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The POM pictures of the azobenzene-dimer were measured when the samples were placed in a cell, which is produced by two glasses. The DSC was measured when the samples were encapsulated in aluminum

box.

The DSC and POM pictures have indicated that the compounds **2b**, **3b** and **4b** all have nematic as they show schlieren texture during the cooling cycle as seen in Fig. S1. To the compound **5a**, the DSC shows that it has two LC phase as shown in Fig. S2a. It can be confirmed by the POM picture, which shows fan texture during the cooling cycle as shown in Fig. S3. What's more, the textures never change as the compound was filled into the cell with vertical orientation, which indicate the fan texture is not the smectic A (SmA). It is hard to find out the exact phase and will be discussed later. Here it was named SmX₁ and SmX₂. To the compound **5b**, it can be found that it has the widest LC temperature range as shown in Fig. S2b. Judging from the POM picture (Fig. S4), it can be found that **5b** shows schlieren texture during the cooling cycle and become an unknown phase, which describes as SmX₃.

3. The influence of azobenzene-dimers on BPs temperature range

Table S1 Compositions, Phase transition and BP temperature range when azobenzene-dimers **5a** and **5b** were doped into BP-LCs.

| Sample No. | Composition | | | Transition temperature/°C | | |
|------------|-------------|-------|------------------------|---------------------------|------|-----------------|
| | Dimer | (Wt%) | LC* ^a (Wt%) | N*-BP | BP-I | ΔT ^b |
| 0 | --- | --- | 100.0 | 37.5 | 43.5 | 6.0 |
| A1 | 5a | 1.0 | 99.0 | 33.0 | 43.1 | 10.1 |
| A2 | 5a | 3.0 | 97.0 | 26.0 | 42.5 | 16.5 |
| A3 | 5a | 5.0 | 95.0 | 26.3 | 42.6 | 16.3 |
| A4 | 5a | 7.0 | 93.0 | 24.1 | 42.8 | 18.7 |
| A5 | 5a | 9.0 | 91.0 | 23.4 | 42.8 | 19.4 |
| A6 | 5a | 11.0 | 89.0 | 29.3 | 43.3 | 14.1 |
| B1 | 5b | 1.0 | 99.0 | 35.8 | 43.2 | 7.4 |
| B2 | 5b | 3.0 | 97.0 | 33.2 | 43.1 | 9.9 |
| B3 | 5b | 5.0 | 95.0 | 26.3 | 43.2 | 16.9 |
| B4 | 5b | 7.0 | 93.0 | 27.8 | 44.6 | 16.8 |
| B5 | 5b | 9.0 | 91.0 | 31.4 | 45.2 | 13.8 |
| B6 | 5b | 11.0 | 89.0 | 35.3 | 46.3 | 11.0 |

^a LC* contains 67%wt% nematic liquid crystal SCL-4 and 33%S811; ^bΔT is the temperature range of BPs

Table S1 shows the compositions, phase transition and BPs range in BP-LCs doped with azobenzene-dimers **5a** and **5b**. The solubility of both azobenzene-dimers can

reach 11%. It can be found that as the increase of azobenzene-dimers, the BPs range also increases. The widest range can reach 19.4 °C for the mixture with 9% **5a**, which is two times more than the mixture without the azobenzene-dimer. And the BPs temperature range of mixture with **5b** can reach 16.9 °C for the mixture with 5% **5b**. it can be found that the azobenzene-dimer **5a** has the greatly influence on the BPs temperature range and has relatively lower clearing point, which is why it was selected for next experiment.

4. The UV absorption properties of the azobenzene-dimers

In order to reveal the absorption properties of the azobenzene-dimers, the UV-Vis spectroscopy of **5a** was measured in CH₂Cl₂ at 25 °C and the corresponding change upon UV and visible light irradiation were studied.

There is two absorption bands show on the UV spectrum of the pure compound **5a** between 300 nm and 500 nm regions, as fig. S5 shows. The one absorption band between 300 nm and 400 nm, which with the maximum absorption at 360 nm (Fig. S5a), is related to π - π^* transition of the azo-chromophore while the other one between 400 nm and 500 nm is related to the n - π^* absorption^[3]. Owing to photochemical *trans* to *cis* isomeration, the maximum absorption of **5a** related to the π - π^* transition band decrease gradually while the n - π^* transition band increase upon UV irradiation, as seen at Fig. S5a. After UV irradiation for about 30 s, the photo stationary state is reached. Moreover, the absorption bands return to the initial state rapidly after irradiation by visible lights about 70 s (Fig. S5b) or stay in the dark for a few hours. The same isomeration properties are found at the other compounds, only with different response time.

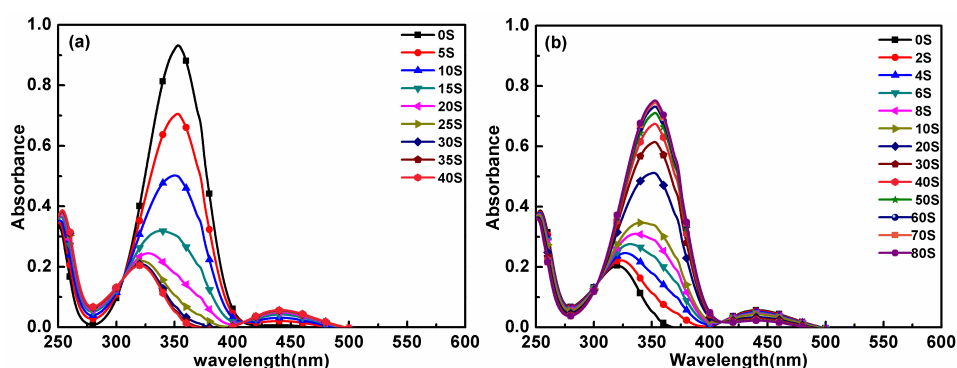


Fig. S5 (a) Absorption spectrum of **5a** and irradiated by UV light; (b) The recovery spectrum of **5a** and irradiated by visible light.

5. The preparation of the Sample to study the effects of trans-cis isomerization of azobenzene-dimers on BPs

The composites of sample A1 were mixed with each other, and then heated up to clearing point and stirred to get a uniform mixture. After that it was filled into a cell make up of two ITO glass and with the thickness of 20 nm. The POM picture were measured when the cell was placed on the heating stage of the Polarized optical microscopy (POM) and the irradiation process was finished on the heating stage. The transmittance spectra were measured with the UV/Vis spectrometer and the cell was also placed on the heating stage and the irradiation process was finished on the heating stage too. All the irradiation process was carried out in dark.

6. The POM pictures and transmittance spectra of the sample A3 when irradiated by UV light (365nm).

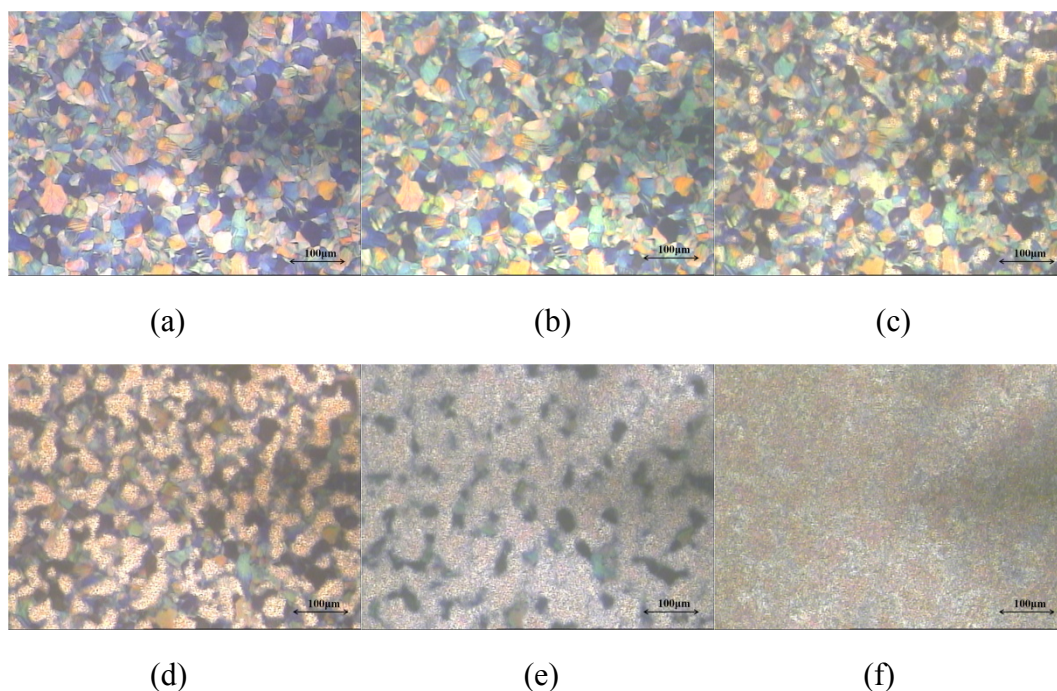


Fig. S6 The POM pictures of the sample A3 and irradiated by UV at 35°C. (a) the irradiated time is 0 s; (b) 10 s; (c) 12 s; (d) 15 s; (e) 20 s; (f) 30 s

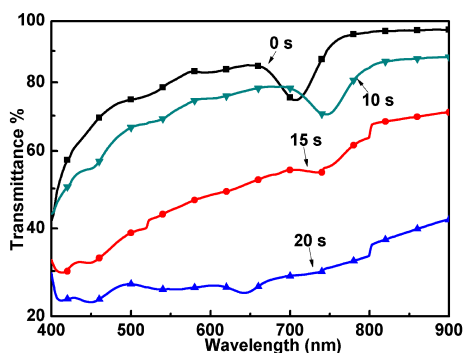


Fig. S7 The transmittance spectra of A3 irradiated by UV at 35 °C

It can be found that the POM picture of the sample A3 change when irradiated by the UV light as shown in Fig. S6. It can be found that the color of BPI texture change as the irradiation time is 10 s and change to N* completely as the irradiation time increase to 30 s. It can be further confirmed by the transmittance spectra of the sample A3 when it irradiated by UV at 35 °C. It can be found that the transmittance peak of BPI red shift in 10s and disappear gradually as shown in Fig. S7.

7. The instruments and materials used in this work

UV/Vis absorption spectra and transmittance spectra were taken with a UV/Vis spectrometer (JASCO, V-570). Polarized optical microscopy (POM) was carried out using an OLYMPUS (BX51) polarizing microscope. The UV irradiation (365 nm) with the intensity of 5.0 mW cm^{-2} and the visible irradiation (450 nm) with the intensity of 5.0 mW cm^{-2} were used in this work. The liquid crystal used in the experiment was SLC-4, a mixed liquid crystal (Yongsheng Huatsing Liquid Crystal Co., Ltd, $\Delta n = 0.235$, $\Delta \epsilon = 29.6$ at 298 K), S811 (Merck Co., Ltd).

References for Supporting Information

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