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Light-controllable reflection wavelength of blue phase liquid crystals doped with azobenzene-dimers†

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A new series of azobenzene-dimers were synthesized and doped into the blue phase liquid crystals to broaden the temperature range of BPs. It is found that not only can the reflection wavelength of BPI be reversibly controlled but BPI can also be transformed into the cholesteric phase owing to isomerization of azobenzene induced by light.

Liquid crystalline blue phases (BPs), which are potentially useful for applications such as fast light modulators or tunable photonic crystals,[1] have attracted considerable attention in recent years due to their intriguing electro-optical characteristics and unique self-assembled cubic structures.[2] According to the difference in their microstructures, BPs can be divided into BPI, BPII and BPIII. BPIII is an amorphous phase with a local cubic lattice structure, while BPI and BPII have a body-centred-cubic structure and a simple cubic structure, respectively.[3] The periodicity of the microstructure, about several hundred nanometres, is on the scale of the wavelength of visible light, so the BPs can produce Bragg reflection around visible light, which is important to the liquid crystal (LC) lasers and other applications.[4] Usually, BPs are found in a very narrow temperature range about 1 °C between the chiral nematic (N*) and isotropic (Iso) phases, which is one of the major obstacles to their practical applications. To overcome the challenge, several methods have been proposed, including stabilizing the BPs with a polymer network[5] or nanoparticles[6] and using low-weight molecules such as T-shaped molecules,[7] dimer molecules[8] and bent-core molecules.[9] Interestingly, H. J. Coles *et al.*[8] have reported that the dimers can stabilize the BPs to a large degree, where the dimers contain two mesogenic units which are linked by a flexible spacer. Due to their special structures, they have attracted growing attention because their mesophase behaviour is clearly different from that of the corresponding monomers.[10] Especially, the dimers with an odd spacer have a bent-shaped structure and show a large flexoelectric effect, which is considered beneficial for the stability of BPs.[11]

Azobenzene compounds have recently given rise to enormous interest owing to their good chemical stability and reversible isomerization between the *trans* and *cis* isomers.[12] The *trans*-isomer, which is linear and thermodynamically stable, is beneficial for the stability of LCs; whereas the *cis*-isomer, which is bent and thermodynamically metastable, destabilizes the LC phase. Depending on the *trans*–*cis* transformation of azobenzene, extensive studies have been carried out to control the orientation of LCs, such as inducing smectic phase transition,[13] adjusting the reflection wavelength of the N* phase[14] or Bragg reflection of BPs.[15] Among them, the tuneable wavelength of BPs is attracting since it can be potentially used in three-dimensional photonic crystals and optically addressable BP-LC displays, which was first studied by H. Y. Liu *et al.*[15] However, the adjustment range mentioned in their report is limited to several tens of nanometres and the reflected color of the LC-BP platelet only changed from brown to green, so there is an urgent need to overcome their limitations.

Herein, we firstly report two series of azobenzene-dimers by combining the structural specificity of a dimer with the optical properties of azobenzene, as shown in Fig. 1. Then, the azobenzene-dimers were separately doped into a BP-LC mixture; it was found that the temperature range of BPs could be broadened to some degree. Importantly, the reflection wavelength of the composite can be successfully controlled under UV or visible light irradiation. As can be seen from the POM picture, the reflected color of the LC-BPI platelet[1,5,7] can be reversibly changed from red to blue, and light-induced BPI to N* phase transition was observed in the BP-LCs doped with a high concentration of azobenzene-dimers, which is potentially used for light-control switches or optically addressable BP-LC displays.

Table 1 displays the phase transition behaviours of the azobenzene-dimers, and the details about their synthesis are shown in the ESI.† It can be found that the azobenzene-dimers with trifluoromethyl linked by an alkyl chain show no mesophases,

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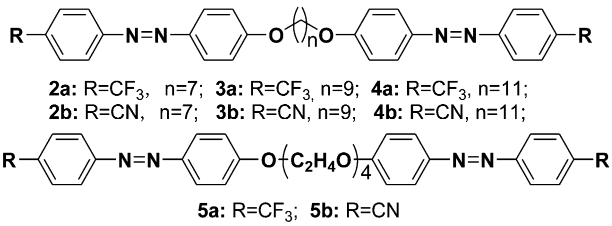

Fig. 1 Structures of the investigated compounds.

Table 1 The phase transition temperature and corresponding transition enthalpies of the azobenzene-dimers

Sample no.	Phase transition during the cooling cycle/(°C, ΔH/kJ mol^{-1})
2a	Iso 149.5(43.8) Cr
3a	Iso 139.1(49.2) Cr
4a	Iso 136.6(55.5) Cr
2b	Iso 221.6(4.0) N 161.4(68.6) Cr
3b	Iso 205.4(2.9) N 147.7(65.7) Cr
4b	Iso 194.1(3.5) N 146.6(73.3) Cr
5a	Iso 114.3(13.7) SmX$_1$ 109.2(4.9) SmX$_2$ 89.0(12.0) Cr
5b	Iso 113.8(0.5) N 67.1(0.8) SmX$_3$ 38.6(8.8) Cr

Iso: isotropic; Cr: crystal; SmX: unknown smectic; N: nematic phase.

while the one with cyano linked by an alkyl chain shows the nematic (N) phase, and with a longer alkyl chain, the temperature range of the N phase is broadened and the clearing point is reduced. This can be attributed to the fact that the trifluoromethyl has a greater lateral volume, which is bad for the ordered arrangement of the compounds, and an increase in the length of the alkyl chain also increases the flexibility of the molecule, which makes it more favourable for the formation of a mesophase. Importantly, all the azobenzene-dimers linked by tetraglycol chains show mesophases, two unknown smectic phases (SmX) for **5a** and an N phase and SmX for **5b**, as the tetraglycol chain is more flexible than the alkyl chain that makes it more favourable for the mesophases and leads to a lower clearing point.

As the azobenzene-dimers **5a** and **5b** have a relatively low clearing point and a wide temperature range of the mesophase, they were chosen to study the influence of azobenzene-dimers on the temperature range of BPs when they were incorporated in BP-LCs, as presented in Table 2 (the details of **5b** can be seen in the ESI†). With the increase of the solubility of azobenzene-dimers, the temperature range of BPs first broadened and then decreased. The widest range can reach 19.4 °C for the mixture with 9% **5a**, which is two times more than that observed for the mixture without the azobenzene-dimers. This can be explained due to the fact that the azobenzene-dimers with an odd spacer have a bent-shaped structure and show a large flexoelectric effect, which are two significant factors to the stability of BPs.[9,11]

Table 2 The liquid crystalline composites prepared and the corresponding BP temperature range when **5a** was doped into BPs-LC

	Composition		Transition temperature/°C		
Sample no.	**5a** (wt%)	BP-LC^a (wt%)	N*-BP	BP-I	ΔT^b
A0	—	100.0	37.5	43.5	6.0
A1	1.0	99.0	33.0	43.1	10.1
A2	3.0	97.0	26.0	42.5	16.5
A3	5.0	95.0	26.3	42.6	16.3
A4	7.0	93.0	24.1	42.8	18.7
A5	9.0	91.0	23.4	42.8	19.4
A6	11.0	89.0	29.3	43.3	14.1

[a] BP-LC: 67% (wt%) SLC-4 and 33% S811. [b] ΔT: BP temperature range.

In order to investigate the effects of *trans–cis* isomerization of azobenzene-dimers on the Bragg reflection of BP-LCs, first, the azobenzene-dimer **5a**, which has the greatest impact on the temperature range of BPs, was selected to study the absorption

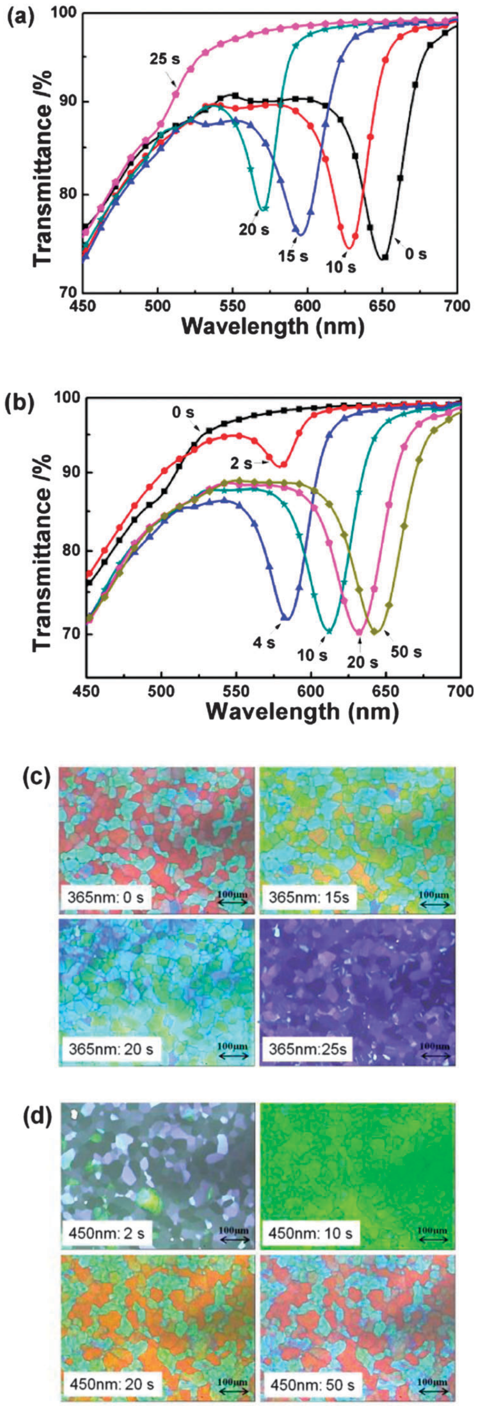

Fig. 2 (a) The transmittance spectral change of the composite A1 when irradiated by UV at 38.5 °C; (b) the transmittance spectral change of A1 when irradiated by visible light after irradiation by UV; (c) change in POM pictures of the composite A1 when irradiated by UV at 38.5 °C; (d) POM picture of A1 irradiated by visible light after irradiation by UV.

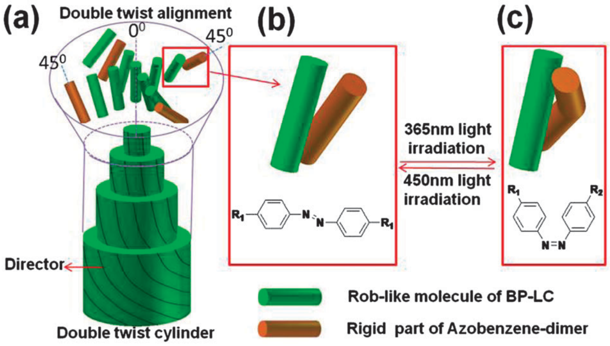

Fig. 3 (a) The possible illustration of azobenzene-dimers doped into the BP-LCs; (b) partial enlargement of the double twist before irradiation; (c) partial enlargement of the double twist after irradiation.

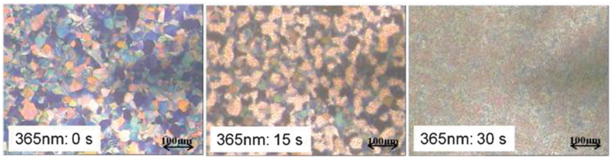

Fig. 4 POM pictures of A3 irradiated by UV at 35 °C.

properties, as shown in the ESI.† Then the transmittance spectra and POM pictures of LC-BPI[1,5,7] doped with 1% of **5a** (sample A1) were obtained under UV (365 nm) or visible light (450 nm) irradiation at 38.5 °C, as shown in Fig. 2. When irradiated by UV light, the transmission peak shifts from 650 nm to a shorter wavelength. It shifts to 625 nm in 10 s, 600 nm in 15 s, 570 nm in 20 s and disappears in 25 s, and then no change is observed as the time increases, as shown in Fig. 2a. On the other hand, when irradiated by visible light, it recovers to the original position rapidly (Fig. 2b). As observed from the corresponding POM pictures in Fig. 2c, the transmittance changes from red to yellow when the irradiation time is 15 s and then changes to green when the time is 20 s and becomes blue in 25 s, after that no change is observed upon increasing the irradiation time, which is consistent with the transmittance spectra. Importantly, the texture of the sample returns to the original color as it is irradiated by visible light, as seen in Fig. 2d.

Fig. 3 is the possible illustration of azobenzene-dimers doped into the BP-LCs and partial enlargement of the double twist alignment when irradiated by light. According to previous research, it can be inferred that the isomerization of azobenzene causes the bending of the rigid part of the azobenzene-dimers,[16] which affects both the molecular order and the 'effective' helical twisting power (HTP) of the mixture[17] and results in the azobenzene-dimers surrounding the rod-like molecules of LC,[18] thus making the LC more compact and resulting in the shrinkage of the double twist cylinder of BPI, which leads to a decrease of the lattice constant. While irradiated by visible light, the *cis*-isomer turns back to the *trans* configuration, which results in the restoration of the Bragg reflection. Some similar phenomena have also been observed in previous publications.[19]

Furthermore, the isomerization of azobenzene-dimers in BPI results in the phase transition from BPI to N*, as shown in Fig. 4, which presents the POM pictures of sample A3 when irradiated by UV at BPI at 35 °C. Upon observing the textures, it can be seen that the irradiation by UV leads to the transformation of BPI into N* when the irradiation time is 15 s and the BPI completely disappears at 30 s, which can be further confirmed by the transmittance spectra, as seen in the ESI.† This can be attributed to the fact that too many *cis*-azobenzenes with a bent-shaped structure cannot be changed to tune the double twist alignment of BPI, thus resulting in the breaking of the double-twist cylinders of BPI, thereby destroying the structure of the BPI, which is consistent with the previous studies.[15,17]

In summary, a new series of azobenzene-dimers were synthesized and their mesophases were found to be mainly affected by the spacers and terminal groups. As they were doped into the BP-LCs, the temperature range of the BPs could be broadened. More importantly, the Bragg reflection of BPI could be controlled effectively and reversibly by light upon introduction of azobenzene-dimers, which can be used to tune the color of BPI from red to blue. Furthermore, the isomerization of azobenzene-dimers can result in the transformation of BPI to N* when irradiated by UV light. This work suggests a new direction for designing molecules that can be used to stabilize blue phases and it is promising for the applications in optically addressable BP-LC displays and other optical devices.

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