

# Broadband reflection of polymer-stabilized chiral nematic liquid crystals induced by a chiral azobenzene compound†

 Cite this: *Chem. Commun.*, 2014, 50, 691

 Received 29th September 2013,  
 Accepted 5th November 2013

DOI: 10.1039/c3cc47438k

www.rsc.org/chemcomm

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**A chiral nematic liquid crystal–photopolymerizable monomer–chiral azobenzene compound composite was prepared and then polymerized under UV irradiation. The reflection wavelength of the composite can be extended to cover the 1000–2400 nm range and also be adjusted to the visible light region by controlling the concentration of chiral compounds.**

The chiral nematic liquid crystal (N\*-LC), which is a nematic liquid crystal (N-LC) doped with chiral molecules, has attracted considerable attention due to its unique reflection characteristics.<sup>1</sup> In a N\*-LC, the long axis of the liquid crystal molecule rotates with periodicity and forms a helical structure. Due to this helical structure, a N\*-LC can selectively reflect circularly polarised light with the same handedness as its helix at a special wavelength range, while the band with the opposite handedness is transmitted.<sup>2</sup> The reflection bandwidth of the N\*-LC is determined using the eqn,  $\Delta n = (n_e - n_o) P = \Delta n P$ , where  $n_e$ ,  $n_o$ ,  $\Delta n$  and  $P$  are the extraordinary refractive index, ordinary refractive index, birefringence and pitch of the N\*-LC, respectively. The pitch, which is the length related to a  $2\pi$  molecular rotation, is influenced by the concentration of the chiral component and reduces with an increase of the chiral fraction.<sup>3</sup> And the value of  $\Delta n$  of the liquid crystal is typically limited to 0.3, so the bandwidth of a single pitch N\*-LC is less than 200 nm in the visible region, which greatly limits its practical applications. Thus, many theoretical studies and experimental methods, which aim at adjusting the pitch of the N\*-LC to get a pitch gradient distribution or a non-uniform pitch distribution to achieve a broadband reflection, have been proposed, such as photo-induced

pitch gradient distribution,<sup>4</sup> temperature-induced non-uniform pitch distribution,<sup>5</sup> nanoparticle-induced non-uniform pitch distribution<sup>6</sup> and non-uniform pitch distribution introduced by mixing the N\*-LC with different pitch.<sup>3</sup> Among them, the photo-induced pitch gradient distribution is widely used since the manufacturing process is simple and practical.<sup>7</sup> Usually, the photo-induced pitch gradient distribution is obtained by mixing the N\*-LC, a photopolymerizable monomer and a light absorbent, and then irradiating them with UV light. Owing to the presence of a light absorbent, a gradient of UV intensity distribution is formed between the lamp side and the other side, thus resulting in a difference in the polymerization rate of the photopolymerizable monomer, and a concentration difference of the photopolymerizable monomer produced, after that a diffusion process starts not only between the photopolymerizable monomer but also the N\*-LC, so a gradient of pitch distribution is formed and is stabilized by the cross-linking of the photopolymerizable monomer.<sup>8</sup> This kind of wideband reflection is very attractive for application in brightness enhancement films,<sup>9</sup> reflective LC displays<sup>10</sup> and other optical applications.<sup>11</sup>

Here, we report the azobenzene chiral compound inducing pitch gradient distribution by combination of the UV absorption properties and changing helical twisting powers (HTPs) of the chiral azobenzene compound (Fig. 1) for the first time. The azobenzene compound has given rise to tremendous interests, such as adjusting the orientation of the LC,<sup>12</sup> controlling the reversibility of encapsulation<sup>13</sup> and making gratings,<sup>14</sup> owing to the good chemical stability and reversible isomerization between the *trans* and *cis* isomers when irradiated by UV or visible light.<sup>15</sup> As it is known, the maximum absorption of azobenzene is at the position of the ultraviolet region, which indicates that the azobenzene compound is a good UV absorbent for the formation of the pitch gradient distribution in broadband reflection. More importantly, the azobenzene group intercalated into the chiral compounds can effectively control the HTPs of the compound upon UV or visible light irradiation, and that the reflection wavelength of the azobenzene-based N\*-LC can be adjusted in the 2000 nm range has been studied extensively.<sup>16</sup> However, whether the reflection wavelength of the azobenzene-based N\*-LC at different UV intensity irradiation can be stabilized

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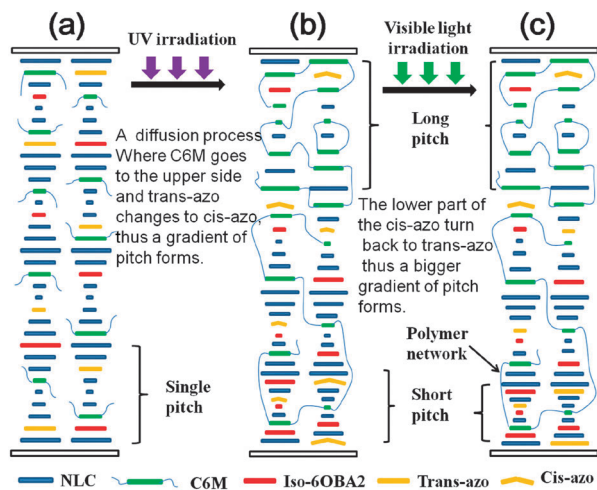
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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3cc47438k

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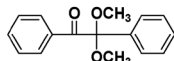
**Fig. 1** The manufacturing process and possible mechanism of the broadband reflection of a polymer-stabilized N\*-LC: (a) the composites filled into the cell and without UV irradiation; (b) the broadband reflection formed after UV irradiation; (c) the broadband reflection with restoration of 2C at the lower side after irradiation by visible light.

by the polymer to form a broadband reflection has never been reported. Here, depending on the superiority of azobenzene chiral compounds, a new method to prepare a broadband reflection is proposed, which can reflect the light covering the wavelength from 1000 nm to 2400 nm and can be adjusted to the visible light region by modifying the HTPs of the composites.

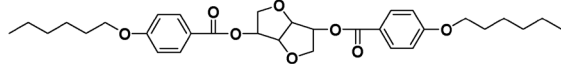
The materials used in this work are listed in Scheme 1. The details of the compounds are given in the ESI.† In the present experiment, to find out the influence of 2C on the pitch gradient distribution, several composites were prepared by mixing the N-LC, Iso-6OBA2,<sup>17</sup> C6M,<sup>3,7</sup> 651 and 2C, as shown in Table 1. The compositions, central reflection wavelengths of the N\* phases and phase transition temperatures of the samples are also listed

(a) N-LC: **SLC-1717** (Yongsheng Huaqing Liquid Crystal Co., Ltd.  $n_o=1.519$ ,  $n_e=1.720$ ,  $\Delta n=n_e-n_o=0.201$ ,  $T_{Cr-N^*}<-40.0^\circ\text{C}$ ,  $T_{N^*I}=91.8^\circ\text{C}$ )

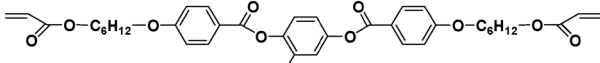
(b) Photoinitiator: **Irgacure 651** (TCI Co., Ltd)



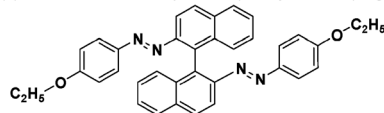
(c) Chiral dopant: **Iso-6OBA2** (Lab synthesized) Right-handed



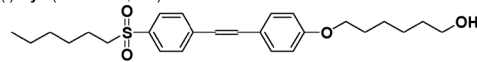
(d) Nematic LC monomer: **C6M** (Lab synthesized) Cr 356.4°C N 388.8°C I



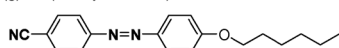
(e) azobenzene Chiral dopant: **2C** (Lab synthesized) Right-handed



(f) Dye (Merck Co., Ltd)



(g) **6C** (Lab synthesized)



**Scheme 1** Chemical structures of the materials used in this work.

**Table 1** The composition and phase transition temperature of the samples

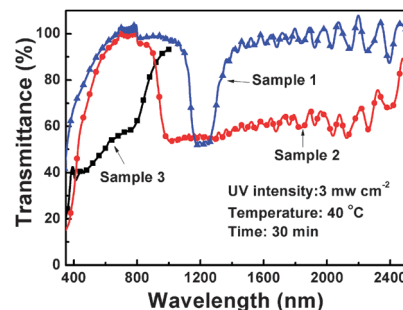
Sample no.	SLC-1717/Iso-6OBA2/C6M/651/2C (wt%)	$\lambda_m^a$ /nm	$T_{Cr-N^*}/^\circ\text{C}$	$T_{N^*I}/^\circ\text{C}$
1	82.05/2.55/15.00/0.40/0.00	1280	-10.0	84.3
2	81.87/2.13/15.00/0.40/0.60	1280	-10.0	83.2
3	78.30/5.70/15.00/0.40/0.60	530	-10.0	65.6

<sup>a</sup> Measured from the transmittance spectra shown in the ESI.  $T_{Cr-N^*}$ : crystal (Cr) to N\*,  $T_{N^*I}$ : N\* to isotropic (I).

in Table 1. It can be found that all the samples have a wide N\* temperature range, and the central reflection wavelengths were kept at the same location as the concentration of 2C increases while the fraction of Iso-6OBA2 decreases slightly.

Fig. 1 shows the manufacturing process and possible mechanism of the broadband reflection of the polymer-stabilized N\*-LC. First, the composites 1–3 were filled into the cell, which consists of two ITO glass with a thickness of 20  $\mu\text{m}$ , as shown in Fig. 1a. And then they were irradiated by UV light (365 nm: 3  $\text{mW cm}^{-2}$ ) at 40  $^\circ\text{C}$  for 30 min, after which the cell was placed under visible light (450 nm 3  $\text{mW cm}^{-2}$ ) for 20 min.

Fig. 2 shows the transmittance spectra of the samples after polymerization. Compared with sample 1 and sample 2, it can be observed that the reflection wavelength of the samples is greatly affected by the fraction of 2C, as shown in Fig. 2. As 0.6(wt)% of 2C is doped into the N\*-LC, the reflection wavelength of the sample after polymerization is broadened, which is about 1400 nm covering 1000–2400 nm, while that of sample 1 without 2C covers the range 1130 to 1310 nm. And the influence of the fraction of 2C on the reflection wavelength can be further confirmed as shown in the ESI.† The mechanism of such broadband reflection can be explained by the formation of a gradient distribution in the helix. As seen from the absorption spectra of 2C in the ESI,† it can be observed that the absorption maximum of 2C located at 360 nm is close to the UV light used in this work. As 2C is doped into the N\*-LC, a gradient in UV intensity is formed over the thickness of the cell, which results in the difference in the polymerization rate at different locations. The upper side of the cell (lamp side) with a strong UV light intensity has a faster polymerization rate, therefore consuming more C6M, while the lower side of the cell with a lower UV light intensity has a slow polymerization rate and consumes less C6M. As the result of different consumptions of C6M, a concentration difference of C6M is produced between the upper and lower sides of the cell. And then the depletion of C6M starts a diffusion process in which the C6M



**Fig. 2** The transmittance spectra of the samples after irradiation by UV light.

diffused to the upper side while the N\*-LC diffused to the lower side.<sup>9</sup> Thus, a helix gradient distribution is realized accompanied with the cross-linking of C6M and the formation of a cross-linked network,<sup>8</sup> as shown in Fig. 1b. More importantly, the isomerization of azobenzene induced by UV irradiation can further expand the reflection wavelength. It can be found that the HTPs of 2C decreased as the UV irradiation time is increased, which exhibits a reflection wavelength of N\*-LC red shift, as shown in the ESI.† So the broadband reflection of the sample shows a red shift owing to the isomerization of 2C under UV irradiation, as shown in Fig. 1b. However, the restoration process takes place when the cell is placed under visible light irradiation for 20 min, which results in the restoration of 2C in the lower side of the cell where the polymer network is rarefaction as shown in Fig. 1c, while the 2C remains at the *cis* isomer at the upper side of the cell where the polymer network is concentrated,<sup>8</sup> so an even bigger gradient of helix is formed, as shown in Fig. 1c. This can be confirmed by comparison to the transmittance spectra of sample 2 before irradiation with visible light as shown in the ESI.† With the fraction of the chiral compound increasing, the reflection wavelength can be adjusted to the visible light region, which covers 400–800 nm, as that of the sample 3 shown in Fig. 2. The transmittance at 400 nm of sample 3 is lower than 50%, which is due to the strong absorbance of the 2C molecule below 500 nm.

To further confirm the influence of azobenzene isomerization on the broadband reflection, a series of comparative experiments were carried out, that is, doping dye, 6C or 2C, into the N\*-LC, respectively, and then polymerizing them under UV irradiation at 40 °C; the details of the composites can be seen in the ESI.† The content of the dopant, which is 1.52%, 0.48%, 0.6% respectively, is determined by the absorptivity.<sup>18</sup> As different fractions of compounds were doped, the absorbance of the mixture is maintained at the same level, so that the same UV gradient distribution is formed. As shown in Fig. 3, which shows the transmittance spectra of the samples after irradiation by UV light, it can be observed that the width of transmittance spectra of the sample doped with 2C is much wider than the one doped with 6C or dye, which can be attributed to the red shift of the broadband reflection caused by the isomerization of azobenzene.<sup>16</sup>

Fig. 4 shows the scanning electron microscopy (SEM) image of the fractured surface of sample 2. It can be found that the sample shows a pitch gradient distribution over the thickness of the cell, that is, a bigger pitch at the upper side while a smaller one at the

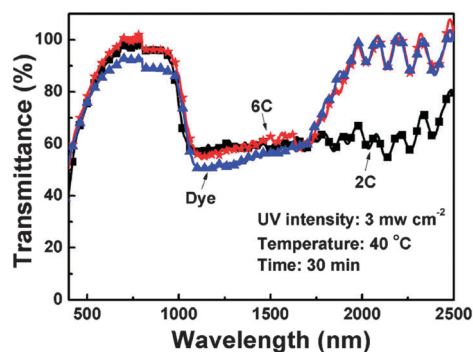


Fig. 3 The transmittance spectra of the sample doped with 0.60(wt)% of 2C, 1.52(wt)% of dye and 0.48(wt)% of 6C.



Fig. 4 The SEM image of the fractured surface of sample 3.

lower side, as shown in the picture: P1>P2>P3>P4. The above experimental results provide an important support for our explanation.

From the above discussion, it can be found that the broadband reflection, which covers 1000–2400 nm in the near infrared region and 400–800 nm in the visible region by adjusting the fraction of the chiral compound before UV irradiation, can be prepared by doping the chiral azobenzene compound into N\*-LC and then irradiating by UV light. This work suggests a new direction for designing broadband reflection and it is promising for the fabrication of wide-band devices.

This work was supported by the National Natural Science Fund for Distinguished Young Scholars (Grant No. 51025313), the National Natural Science Foundation (Grant No. 51333001, 51173003, 51272026, 51273022, 51073096, and 61007016), the Major Program of Chinese Ministry of Education (Grant No. 313002), the Major Project of Beijing Science & Technology Program (Grant No. Z121100006512002), and the Defense Industrial Technology Development Program (Grant No. B1120110006).

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