

# Light induced generation of stable blue phase in photoresponsive diphenylbutadiene based mesogen†

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**Light induced isothermal phase transition leading from smectic A\* phase to a stable blue phase was achieved via photoisomerization of a chiral diphenylbutadiene based mesogen.**

Blue phases (BP) are an interesting class of chiral liquid crystals possessing a fluid lattice which self-assemble into three-dimensional cubic defect structures.<sup>1</sup> The periodicity of these defect structures is of the order of the wavelength of visible light, resulting in interesting optical properties such as selective reflection of circularly polarized light.<sup>2</sup> These properties combined with the ability to reorientate the molecules in blue phases using external electric fields makes them very attractive for applications such as fast light modulators and tunable photonic crystals.<sup>3</sup> In view of this there have been several efforts in designing materials exhibiting thermally stable blue phases, including the use of polymeric and hydrogen bonded systems.<sup>4</sup> Since a clear structure property relationship for this class of materials is yet to be established, methods for generation of the rarely observed blue phase is attracting significant attention. An interesting method for generation of frustrated liquid crystalline phases is to design photoresponsive liquid crystalline materials from molecules which can undergo structural transformation following absorption of light. Although there have been several reports on the generation of chiral nematic phases, including twist grain boundary phases using such photoresponsive liquid crystals,<sup>5</sup> reports on the photogeneration of the blue phase are limited.<sup>6</sup>

In a series of earlier studies we have shown that diphenylbutadiene forms a versatile chromophore for the design of liquid crystals capable of undergoing photoinduced isothermal phase transitions.<sup>7</sup> The photoisomers formed from these systems are thermally stable, and hence the design of chiral photoresponsive diphenylbutadiene based mesogens would be an interesting method of introducing defect structures leading to the formation of frustrated chiral liquid crystalline phases.

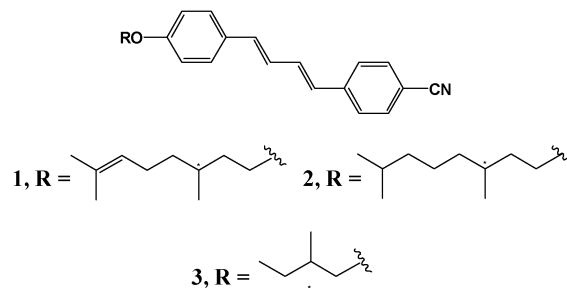
With this objective we synthesised a series of chiral diphenylbutadiene derivatives (Chart 1). None of the derivatives showed a blue phase in heating or cooling cycles. Photoirradiation of the smectic phase of **1** however, resulted in the formation of a

stable blue phase. To the best of our knowledge such photoinduced generation of the blue phase has not been reported before in single component LCs. Films drawn from inherently photoactive LCs can exhibit much faster switching times and enhanced stability compared to doped films.<sup>6,8</sup> The blue phase which could be generated from the SmA\* phase by irradiation with low intensity 360 nm light ( $0.6 \text{ mW cm}^{-2}$ ), had a significantly wide temperature range and its Bragg reflection could be tuned by varying the irradiation time.

The mesomorphic properties of the chiral butadienes were investigated by polarized optical microscopy (POM), differential scanning calorimetry (DSC) and temperature dependent small angle X-ray diffraction (SAXRD). The phase transition properties of these compounds are summarized in Table 1.

The diphenylbutadiene derivative (**1**), exhibited enantiotropic LC phases, with a smectic A\* phase (SmA\*) characterized by focal conic texture appearing at 120 °C (Fig. 1a) in the heating cycle. XRD analysis of the sample at this temperature indicated formation of a bilayered smectic phase (Fig. S2†). On increasing the temperature to 126 °C the SmA\* phase transformed into a N\* phase characterized by its Grandjean texture (Fig. 1b), which was further confirmed using a wedge cell in which Cano lines were clearly visible (Fig. S4†). The characteristic reflection spectra of the N\* phase could be tuned from 560 nm to 740 nm by varying the temperature from 131 to 125 °C (Fig. 2) in the cooling cycle. Further heating of the sample resulted in isotropization at 132 °C. In the cooling cycle a twist grain boundary A\* (TGBA\*) phase was observed at 124 °C (Fig. 1c) in addition to the other phases (Table 1). Phase transition temperatures were further confirmed by DSC (Fig. S1†).

POM studies of **2** on the other hand indicated the formation of a monotropic chiral nematic phase (Table 1). Cooling its isotropic phase to 151 °C resulted in the appearance of an oily



**Chart 1** Structures of the chiral diphenylbutadienes investigated.

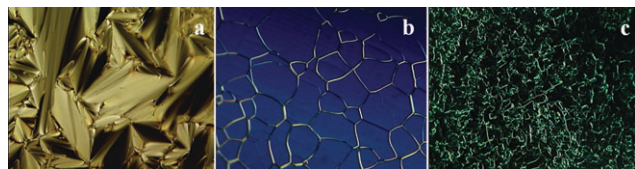
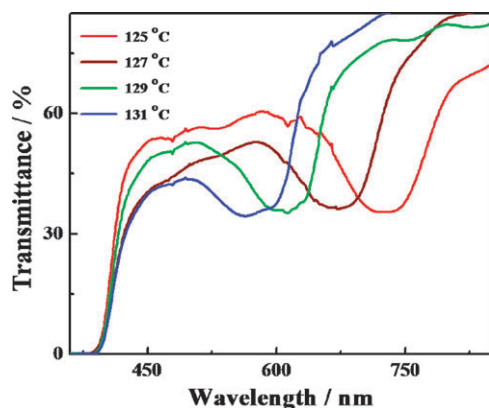
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**Table 1** Phase transition temperatures of the chiral diphenyl butadienes

	Heating cycle, °C	Cooling cycle, °C
1	Cr 120 SmA* 126 N* 132 I	Iso 131 N* 124 TGBA* 123 SmA* 110 Cr
2	Cr 162 Iso	Iso 151 N* 143 Cr
3	Cr 135 SmA* 141 Iso	Iso 141 SmA* 122 Cr

**Fig. 1** Textures of compound **1** at: (a) SmA\* (120 °C), (b) N\* (128 °C) and (c) TGBA\* (123.5 °C), in the cooling cycle.**Fig. 2** Dependence of N\* reflection band, of a 10 μm thin film of **1** on temperature in the cooling cycle.

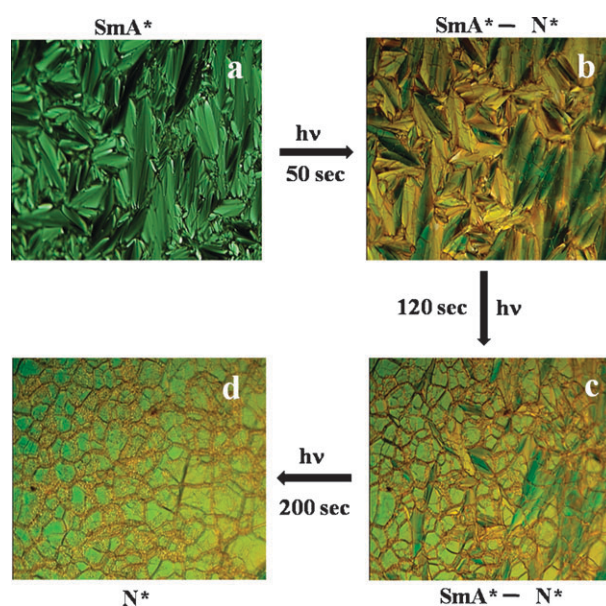
streak texture with selective reflection of light, characteristic of the chiral nematic (N\*) phase. The derivative **3**, which is structurally similar to **1** (Chart 1), did not exhibit any chiral nematic phases, with only a SmA\* phase being observed in its heating and cooling cycles.

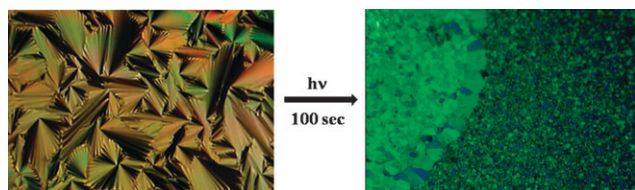
Cyano substituted diphenylbutadiene derivatives have been reported to undergo photoisomerization in solution, liquid crystalline phases and in solid films to form thermally stable *cis* isomers.<sup>9</sup> Photolysis of **1** in acetonitrile using 360 nm light resulted in a substantial decrease in the intensity of its major absorption band centered at 360 nm, with a concomitant increase in intensity of the short wavelength absorption band around 266 nm (Fig. S5†). These changes could be attributed to the *trans*–*cis* photoisomerization of the butadiene chromophore.<sup>9</sup> The *cis* isomers (*EZ* and *ZE*) formed on photoirradiation were isolated using HPLC and characterised by <sup>1</sup>H NMR spectroscopy. On photoirradiation, as the concentration of the *cis* isomers increased, some of the light was absorbed by them resulting in competing forward and backward photoisomerization reactions until a photostationary state was reached, where the concentration of each species was determined by the relative efficiencies of each of these processes. HPLC analysis indicated a ratio of 52/40/8 for the *EE*/*EZ*/*ZE* isomers at the photostationary state of **1** in acetonitrile. <sup>1</sup>H NMR spectral analysis clearly indicated that the peripheral double bond in the alkoxy chain had not undergone isomerization upon 360 nm light illumination.

The linearly shaped *trans* isomers of diphenylbutadiene derivatives are known to exhibit stable LC phases whereas their corresponding bent *cis* isomers do not. Thus photoirradiation of the diphenylbutadiene mesogens can lead to destabilization of their LC phases.<sup>9</sup> Photoinduced isothermal phase transitions of LC phases of **1** were investigated by irradiating its films held at different temperatures with 360 nm light. Photoirradiation of a film of **1** cooled to 118 °C from its isotropic phase (Fig. 3a) for 50 s, resulted in disappearance of the focal conic texture of the SmA\* phase and concomitant appearance of an oily streak texture characteristic of the cholesteric phase (Fig. 3b), which was confirmed by the observation of Cano lines in a wedge cell. On further irradiation (200 s) complete conversion of the smectic phase to N\* phase was observed (Fig. 3d).

Subsequent irradiation did not lead to any further textural changes, indicating that the photostationary state had been attained. HPLC analysis of the film irradiated for 200 s at 118 °C indicated that the photostationary state contained 6% of the *cis* isomers. Photoirradiation of the SmA\* film held at a higher temperature (124 °C), for 100 s, resulted in its transformation to a phase with a characteristic classical blue phase texture shown in Fig. 4 (also see Fig. S3†).

Additionally the characteristic sharp reflection bands (Fig. 5) compared to the rather broad reflection bands observed for the chiral nematic phase confirmed the formation of the blue phase. When the material held in the SmA\* LC state at 124 °C in the heating cycle was irradiated with 360 nm light for 100 s, photoinduced formation of the *cis* isomer

**Fig. 3** Photoinduced isothermal phase transition of **1** at 118 °C on irradiation with 360 nm light.

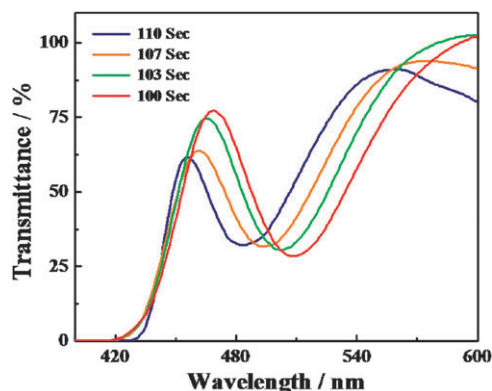


**Fig. 4** Photoinduced isothermal phase transition of compound **1** from SmA\* to blue phase at 124 °C on irradiation with 360 nm light.

resulted in the formation of the blue phase and the reflection band was centred at 510 nm. Subsequent irradiation led to the blue shift in the reflection band. The blue phase thus formed was thermodynamically stable and could be maintained at this state for several hours. On heating, this phase underwent isotropization at 128 °C.

The texture displayed in Fig. 4 clearly exhibits the mosaic platelet pattern, ruling out the photoinduced BP being of the BPIII (fog phase) type and indicating a cubic structure BP *i.e.*, either BPI or BPII. It is known that the temperature dependence of the selective reflection wavelength  $\lambda_{\text{max}}$  decreases significantly with increasing temperature in the BPI phase,<sup>2,3</sup> but has a negligible or at best a weak positive variation in the BPII phase. Since the appearance of the BP in the present experiments is temporal *i.e.*, time elapsed since the beginning of *trans*–*cis* isomerization, it is akin to increase in temperature. The data in Fig. 5, where  $\lambda_{\text{max}}$  exhibits strong time dependence suggests that the photoinduced phase is BPI.

HPLC analysis of the film irradiated for 100 s indicated that the total content of the *cis* isomers in this mixture to be 17%. The formation of the blue phase on photoirradiation of the film held at 124 °C, and its absence in films held at 118 °C, can be attributed to the increased amounts of *cis* isomers formed at the higher temperature as a result of the lowered viscosity of the smectic phase close to its smectic A\*–N\* phase transition



**Fig. 5** Changes in the transmittance spectra in the blue phases generated by the photoillumination of a film of **1** at 124 °C on irradiation with 360 nm light.

temperature. Photoisomerization of the *trans* isomers of polyenes is known to be very sensitive to viscosity, decreasing drastically with increasing viscosity.<sup>10</sup> Further irradiation led to isotropization of the sample where the *cis* content was 24%.

In conclusion, chiral mesophases could be generated by covalently attaching alkyl chains containing asymmetric carbons to the diphenylbutadiene moiety, whose nature and stability depended upon the nature of the alkyl chain. Photochemically generated *cis* isomers of the diphenylbutadiene derivative **1** resulted in isothermal phase transitions from smectic A\* to stable chiral phases such as the chiral nematic and blue phases depending upon the extent of photoisomerization. Further investigations are in progress on increasing the stability of the photochemically induced blue phases.

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