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Photoactive dimesogen having different pathways of light driven phase transitions at different temperatures

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We hereby describe a novel example of light driven phase transitions in a photoresponsive dimesogen, which goes through different pathways at different temperatures. The isomer ratios required to obtain the phase transition in each case have also been determined.

Photonics in which light can be controlled with light as a stimulus is being proposed as a future technology for high speed information processing.[1,2] Photoresponsive liquid crystalline (LC) materials are particularly suited for such applications since their liquid like nature provides the possibility of molecular motion in response to the properties of light. Light driven reversible phase transition in LCs has received considerable attention in recent years due to the drastic change in their optical properties upon phase transition, which can be used for the fabrication of new molecular devices or optical image recording systems.[1–5] Various kinds of photo induced phase transitions including nematic–isotropic,[3,4] smectic A–isotropic,[6,7] smectic A–chiral nematic,[8] nematic–chiral nematic,[9–11] chiral smectic C–chiral nematic[12] and chiral smectic C–smectic A[13] have been reported.[14] We describe herein the first successful demonstration of light driven phase transitions in a photoresponsive dimesogen (**7n8**) having multi routes at different temperatures. This molecule exhibits a chiral smectic C (SmC*), a chiral smectic A (SmA*) and a chiral nematic phase (N*) in the heating and cooling cycles. Photoirradiation in the SmC* phase resulted in the direct transformation into an isotropic phase without changing to the intervening low order SmA* and N* phases, which are present at the higher temperatures. Irradiating in its SmA* phase, an N* phase has been observed that on further irradiation turned into an isotropic phase. To the best of our knowledge previous literature reports on photochemical phase transition in the LCs (other than chiroptical switches) have shown to exhibit the same photo induced phase transition trend as their thermal phase change.[14]

The dimesogenic compound investigated in this study has been prepared as described in the synthesis of related compounds.[8,15] Table 1 summarizes the phase transition temperatures in the heating and cooling cycles. On heating, the compound melts to a SmC* phase confirmed from its characteristic broken fan shaped texture with dechiralization lines, schlieren texture (Fig. 2a) and also the reflecting nature of visible light. Small angle X-ray diffraction (SAXRD) studies show Bragg diffraction peaks in the small angle region, corresponding to the layer reflection and a diffuse peak in the wide angle region due to the liquid like order in the smectic layers. The two peaks (more and less intense) at the small angle region[8,16] correspond to two kinds of arrangement in the smectic liquid crystalline phase (Fig. 1). The molecular length of **7n8** has been calculated to be 51.4 Å. Also, as observed for reported SmC* phases, layer spacing at a lower angle was found to be decreased upon lowering the temperature due to the increase in the tilt (Fig. 1, inset).[17] (More details on the SmC* phase are under investigation). On heating, a phase change to SmA* has been observed, which is confirmed by its homeotropic focal conic texture. In the SmA* phase also, SAXRD exhibits two reflections in the small angle region (Fig. 1b). Interlayer distances (d) calculated for the more and less intense peaks at lower angles are 23.6 Å (d/L = 0.46, where L is the length of the molecule), intercalated arrangement[16] and 46.6 Å (d/L = 0.91), monolayer arrangement respectively. From the X-ray diffractogram it is clear that in the SmA* phase, the intercalated arrangement is more stabilized; it is also important to note that in the SmC* phase, the monolayer arrangement (tilted) is more favorable (Fig. 1). On further heating from the SmA*, a phase transition to N* has been observed that has been confirmed by a Grandjean texture using polarizing optical microscopy.

Thin layers of the dimesogen were sandwiched between cover slips containing 5 μm glass spacers and the film was heated to the isotropic temperature and slowly cooled to 100 °C. At this temperature the compound exhibited a schlieren texture of SmC* (Fig. 2a). Upon irradiation of the film using 366 nm light obtained from a high-pressure mercury lamp for 60 seconds, the SmC* phase underwent a transition to an isotropic phase. Partial isomerization of the azo moiety present in the **7n8** has taken place from the *trans* to the *cis* form on irradiation. The *trans* form of the azobenzene stabilizes the LC phase due to its rod like nature and the *cis* form destabilizes the LC phase due to its bent shape and thus *trans* to *cis*

Table 1 Phase transition temperatures and enthalpies of the dimesogen **7n8**

	Phase transition temperature/°C,[a] (ΔH/kJ mol^{-1})
Heating	Cr 86.6 (25.6) SmC* 110.6 (0.5) SmA* 126.2 (0.1) N* 159.3 (4.0) Iso
Cooling	Iso 155.0 (4.3) N* 125.2 (0.1) SmA* 106.4 (0.5) SmC* 66.6 (22.5) Cr

[a] Cr = crystalline, SmC* = chiral smectic C, N* = chiral nematic, SmA* = chiral smectic A and Iso = isotropic.

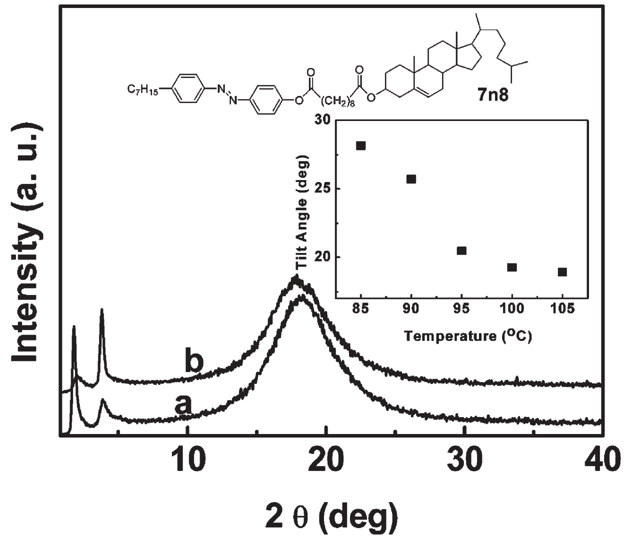

Fig. 1 The intensity profile of the X-ray diffraction pattern exhibited by the dimesogen (a) at 100 °C (cooling cycle), (b) at 120 °C (cooling cycle). Inset shows the plot of temperature *versus* the tilt angle in the chiral smectic C phase.

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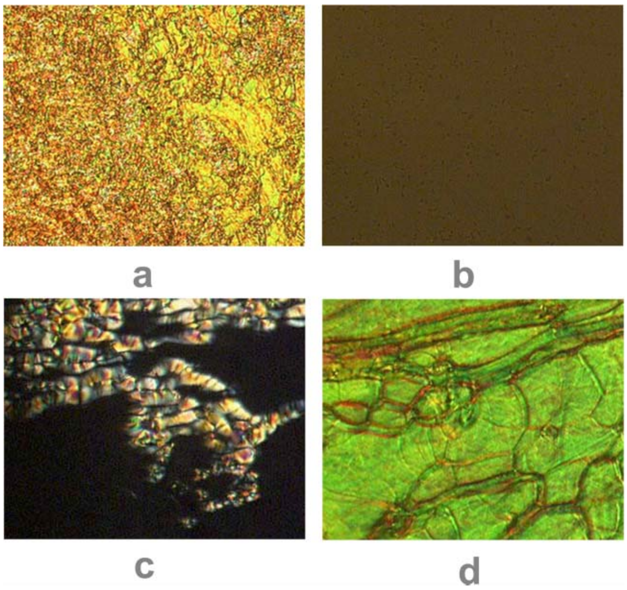

Fig. 2 Optical photographs of the dimesogen in the cooling cycle (a) at 100 °C before irradiation, SmC*, (b) at 100 °C, after irradiation for 60 seconds using 366 nm light, isotropic, (c) at 120 °C, before irradiation, SmA* (d) at 120 °C, after irradiation for 30 seconds using 366 nm light, N*.

isomerization causes the phase transition. In the process of light induced phase transition, low order SmA* and N* phases present in the LC system have not been seen. The obtained isotropic phase after the irradiation has been found to reverse to the SmC* phase in 120 seconds due to the *cis* to *trans* back isomerization (at 100 °C, cooling cycle). In the reversal process also, N* and SmA* phases were found to be absent. This is further confirmed by irradiating SmC* to the isotropic phase and suddenly heating the film to 120 °C (the temperature of SmA*). In this experiment the isotropic phase was firstly turned into the N* phase, which changes to the SmA* (in 40 seconds). For further investigation of the photoinduced phase transition, thin layer of **7n8** has been irradiated in its SmA* phase at 120 °C (cooling cycle, for 30 seconds) (Fig. 2c). Isomerization of the *trans* form of the azo moiety to its *cis* form changes the phase to an N*, which has been confirmed by the appearance of a Grandjean texture (Fig. 2d). After continuous irradiation for 300 seconds, the generated N* phase has been changed into an isotropic phase. These light driven phase transitions have also been found to be completely reversed due to back *cis* to *trans* isomerization (in 45 seconds). To study the percentage of the *cis* isomer of **7n8** required for the light induced phase transition, detailed HPLC experiments were conducted. For the HPLC studies, a thin film (5 μm) of **7n8** was irradiated for the time required for the phase transition and after obtaining the phase change the film was suddenly quenched to room temperature. At room temperature the *cis* to *trans* reverse isomerization rate is found to be very slow. It has been observed that for the formation of an isotropic phase from the SmC* phase (at 100 °C, cooling cycle) 30% of the *cis* isomer is required. In the SmA* to N* and SmA* to isotropic photo induced phase transitions at 120 °C (cooling cycle), the ratio of *trans* : *cis* isomer has been found to be 94 : 6 and 81 : 19 respectively. We have done the photo induced phase transitions at different temperatures such as 90 (SmC*), 100 (SmC*), 115 (SmA*), 120 (SmA*), 130 (N*) degrees and the ratio of the isomers required for the change of LC phase have been determined. A binary phase diagram has been plotted with the percentage of *cis* isomer on the *x*-axis and temperature on the *y*-axis (Fig. 3). The isotropic–LC phase transition temperature has been found to decrease upon increasing the *cis* content in the mixture. For example, the percentage of *cis* isomer required for the N*–isotropic phase transition at 130 °C has been found to be 7%, which means that a binary mixture of *trans* : *cis* (93 : 7) decreases the isotropic–LC temperature by 25 °C. On increasing the *cis* ratio, the same trend has been observed for the N*–SmA* phase transition (Fig. 3). From the binary phase diagram it can also be seen that the SmA* to SmC* transition temperature deviates from the general observation (upon photoirradiation of the SmC* phase, an isotropic phase is observed), which follows the straight line. This may be explained by taking into account the molecular orientation in the SmC* and SmA* phases in the dimesogen. X-Ray studies have shown that the SmC* phase exists as tilted monolayers. Molecular orientation in the SmA* phase has been found to be intercalated (Fig. 1). Since the alternation from the monolayer to intercalated arrangement needs the sliding of one molecule against the neighboring molecule by weakening the interactions between two pairs of mesogens, the photochemical isomerization of just one of the mesogens is insufficient to induce this rearrangement. This could be the reason for the direct change from the SmC* phase into the isotropic phase upon photoirradiation. In the heating and cooling process, tilted monolayers of SmC* transforms to the intercalated phase due to the vibration motion of the molecule. In the case of phototransformation from SmA*, interactions with the one pair of mesogens in the intercalated arrangement weakens due to the formation of a bent *cis* isomer, which favors the formation of a cholesteric phase. In summary we have demonstrated the photoinduced phase transition in a polymesomorphic dimesogen. Dimesogens are potential candidates for photonic applications. We are currently exploring more on these materials.

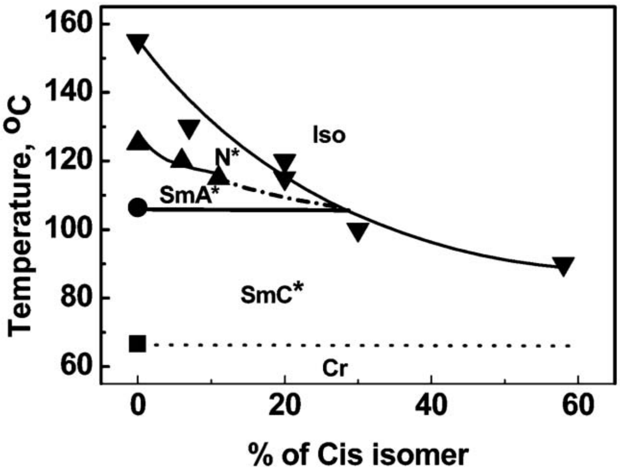

Fig. 3 Binary phase diagram obtained by the photogeneration of the *cis* isomer of **7n8**.

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