

Design of chiral dimesogens containing cholesteryl groups; formation of new molecular organizations and their application to molecular photonics

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Photoresponsive liquid crystals and organogels are finding increasing application in information technology and photonics. In this *tutorial review*, the authors describe how weak intermolecular interactions facilitate molecular organization of cholesterol-containing dimesogens to form such materials. Design considerations and photoresponsive properties of both organogels and glassy liquid crystals are discussed and their applications to molecular photonics highlighted. The review will be of value to readers interested in the development of new materials which respond to the different properties of light.

1 Introduction

Recently a lot of interest has been paid to basic and applied studies on molecular organizations formed by relatively weak intermolecular interactions such as hydrogen bonding and van der Waals forces.¹⁻³ Some molecules self assemble to form molecular organizations showing new optical or electrical properties, which were not observed in the single molecule. Since weak interactions are sensitively influenced by external stimuli such as light, temperature and electric field properties of these molecules can be easily controlled. Liquid crystalline systems and organogels are some examples of these molecular organizations. Liquid crystals are compounds which show both the property of a well arranged crystal and highly disordered liquid state. The organo gel state can be defined as solvent molecules trapped in a network of solute due to weak molecular interactions like hydrogen bonding, van der Waals forces or π -stacking.

Dimesogens/dimers/twins (liquid crystals containing two mesogenic units linked through a flexible spacer) have attracted much

attention because they exhibit new liquid crystalline phases, serve as useful models for semi-flexible, main chain liquid crystalline polymers⁴ and show unique properties applicable for new optical materials. Dimesogens can be considered as the lowest possible oligomer and exhibit some characteristic properties of polymers such as glass transition. Glassy liquid crystals are materials which constitute a state of matter wherein the long-range molecular order of liquid crystals is frozen into the solid state. Most low molar mass liquid crystals will crystallize upon cooling from the melt. But there are some exceptions in which organic liquid crystalline compounds transform to glassy liquid crystals on sudden cooling. Molecules showing slow reorientation to crystalline structure are suitable for obtaining glassy liquid crystalline materials. The combination of optical properties of liquid crystals and mechanical properties of solids make glassy liquid crystals exclusively suited for a variety of practical applications.^{5,6} A high viscosity or three dimensional network of polymeric chains practically forms a glassy liquid crystalline state, but the reversible fast switching which is required for application purposes is impossible because of its high molecular

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Nobuyuki Tamaoki was born in Japan in 1959. In 1982 he graduated from Chiba University. After working at the Toyobo Co. research center, he commenced his doctoral studies in 1989 with Professor Tsuguo Yamaoka at Chiba University, where he was awarded his PhD in 1992 for work on the photochromism of macrocyclic azobenzene derivatives. In 1992, he joined the Research Institute for Polymers and Textiles (now National Institute of Advanced Industrial Science and Technology) where, since April 2000, he has been a group leader in the Molecular Function Group. He was also a visiting research associate from 1995 to 1996 with Professor M. Reza Ghadiri at the Scripps Research Institute in the United States. His research is mainly focused on photoresponsive molecular organizations. He is also interested in molecular design, synthesis, and function of macrocyclic compounds such as catenanes, rotaxanes, and cyclic peptides.



weight. Low molecular weight compounds such as dimesogens are appropriate for this function. In this article we present a brief account on the vitrifiable chiral dimesogens containing cholesteryl moieties and also dimeric molecules which form photoresponsive organogels. Chiral dimesogens containing cholesteryl groups have been extensively investigated for structure–property relationships.⁴ But this review mainly focuses on cholesteryl containing dimesogens which are potential candidates for applications in molecular photonics or information technology.

Before considering the details of these aspects it is appropriate to describe the importance of cholesteryl groups in the formation of molecular interactions generating liquid crystals as well as organogels.

2 Importance of cholesteryl groups in the formation of novel materials

Cholesterol (Fig. 1) is abundant in nature and a commercially available chiral compound. The main interest behind the designing of new materials containing cholesteryl groups results from its

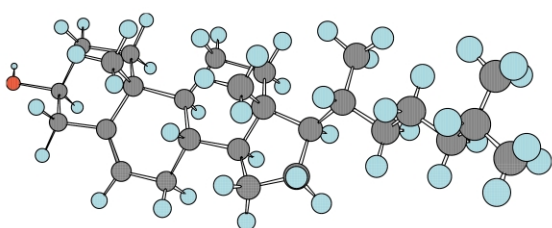


Fig. 1 Structure of cholesterol.

rigid-long shape and chiral structure. Rigid-long shape induces large intermolecular interactions *via* van der Waals forces stabilizing parallel molecular stacking. The chiral structure induces chirality in molecular order, namely helical superstructure. In the field of liquid crystals, from the time of their discovery cholesterol containing liquid crystals have fascinated researchers because of their distinct optical properties.⁷ Liquid crystalline phases of calamitic compounds can be roughly divided into nematic, cholesteric (chiral nematic) and smectic depending on the type of molecular alignment. In a smectic phase, molecules are not only parallel but are also arranged in such a way that the centers of adjacent molecules lie in a plane (Fig 2a). In a nematic mesophase,

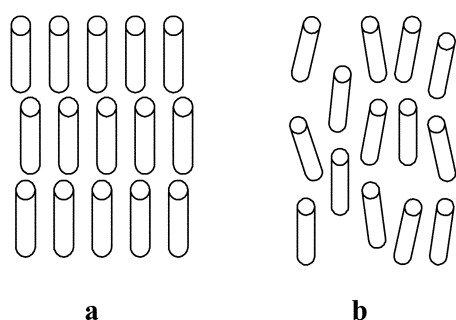


Fig. 2 Schematic representation of the molecular order in (a) smectic A liquid crystal (b) nematic liquid crystal.

the molecules are aligned with their long axes parallel to each other (Fig 2b). and in cholesteric mesophase, thin nematic layers are stacked with their directors rotated forming helical ordering as shown in Fig. 3.

Optical properties of cholesteric phases are due to the presence of helical super-structure (Fig. 3). The molecular ordering of cholesteric liquid crystals in helical arrangement induces reflection of circularly polarized light at the wavelength satisfying the equation $\lambda_{\max} = p n$, where λ_{\max} is the reflection maximum, p is the pitch of the helix and n is the refractive index. Pitch length of a cholesteric liquid crystal can increase or decrease with temperature depending

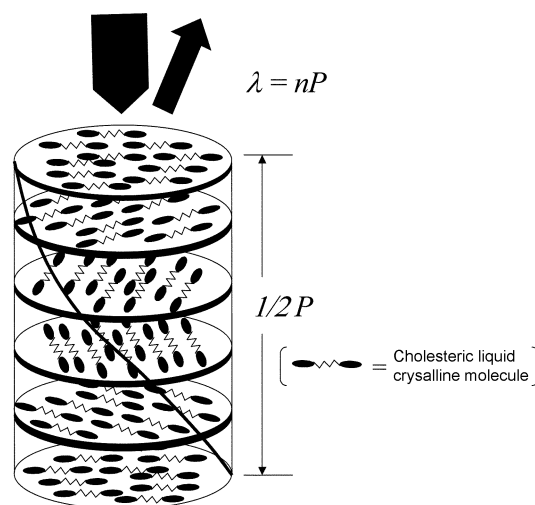


Fig. 3 Diagram of the helical structure of cholesteric liquid crystal.

on the sign of thermal coefficient α , which is equal to $1/p [dp/dT]$, where p is the pitch length and T is the temperature. When $[dp/dT] > 0$ pitch length will increase with increasing temperature and *vice versa*. Reflected color of cholesteric liquid crystals generally depends on the chemical structures of liquid crystalline molecules, nature and concentration of the doped impurities, temperature and electric field.

In the field of the organogels also, cholesterol containing compounds are well explored.^{8,9} In cholesterol containing compounds van der Waals forces may play an important role in stabilizing the one dimensional molecular organization.

3 Design and study of glass forming chiral dimesogens

3.1 Dimesogens forming cholesteric glassy liquid crystals

There are many reports within polymeric systems on the fixation of the cholesteric molecular ordering by sudden cooling or cross linking,⁶ whereas the number of low molecular liquid crystals forming stable glassy cholesteric order is limited.^{6,10,11} We observed that dimesogens containing two cholesteryl groups linked with diyne and alkyl chain can be reversibly solidified maintaining the reflected cholesteric colors between two glass plates (Fig. 4).^{12,13} In addition, the color of the reflection band of the compound

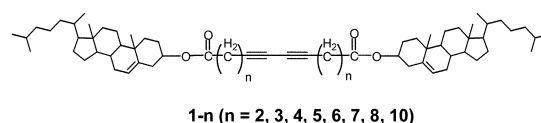


Fig. 4 Structures of glass forming dimesogens.

can be selected from the entire visible region (Fig. 5). The dicholesteryl ester exhibits a monotropic cholesteric phase (liquid crystalline phase only in cooling cycle) showing reflected colors from blue to red, depending on the temperature and cooling rate. When the compound was quickly cooled to 0 °C, it solidified maintaining the iridescent color at which quick cooling started (Fig 5). The colored cholesteric glassy liquid crystalline film was found to be stable for more than 5 years at room temperature. These cholesteric glassy liquid crystalline phases are found to be stable up to about 70 °C. Rewritable full color recording could be achieved from these materials (Fig. 6). Ease of fixing the cholesteric colors, the region of fixed reflection bands and thermal stability of cholesteric glassy liquid crystalline states were highly dependent on the length of methylene units in the molecules. Cholesteric glassy liquid crystals obtained from dimesogens linked by an even number of methylene units show more stability than those linked by an odd number of methylene units. In order to find the origin of

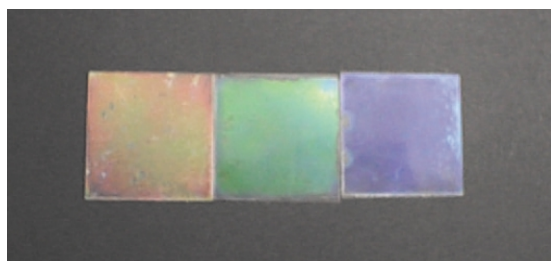


Fig. 5 Photographs of cholesteric glassy liquid crystalline films obtained from **1-8** quenching at different temperatures. (Reproduced from ref. 12 with permission from Wiley-VCH.)

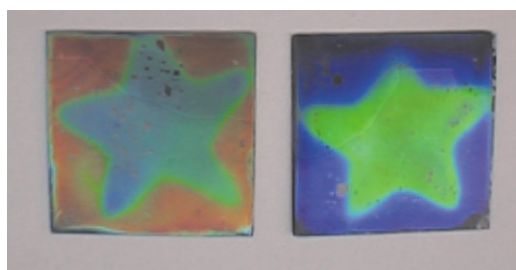


Fig. 6 Photographs of stars recorded in the cholesteric glassy liquid crystalline films obtained from **1-8**. (Reproduced from ref. 12 with permission from Wiley-VCH.)

interactions between molecules which stabilize cholesteric structure, infrared spectra of the cholesteric glassy liquid crystal and crystalline states were compared for different alkyl chain lengths (Fig. 7). From these studies it can be concluded that carbonyl

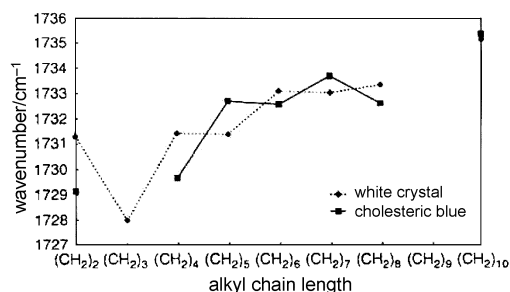


Fig. 7 Vibrational frequency of carbonyl linkages in **1-n** in the crystalline state and cholesteric glassy liquid crystalline state.

groups of the compounds linked by an even number of methylenes exist in a more dipolar electronic structure in the cholesteric glassy liquid crystalline state compared to the crystalline state. In compounds having an odd number of methylene spacers, the opposite effect to this is seen. Thermal properties of symmetrical dimesogens containing two cholesteryl moieties and different linkers have been investigated (Fig. 8).⁶

Cholesteric glassy liquid crystals showing different colors can also be obtained by coating from the solution of these dimesogens, **1-n**. If 15wt% solution in dichloromethane is spin coated at 7000 rpm on a glass plate at 22–23 °C, it forms a red cholesteric glassy liquid crystalline film.¹⁴ Changing the temperature of the substrate allows the control of the fixed color (Fig. 9). Fig. 10 shows the relationship between the temperature of the substrate during the spin coating and the wavelength of the reflection band. The peak shifts toward longer wavelengths (530 to 832 nm) as the substrate is cooled from 40 °C to 2 °C. The color observed in the glassy liquid crystalline film also depends on the structure of the dimesogen used as well as the organic solvent.

3.2 Cholesteric glassy liquid crystals from supramolecular hydrogen bonded systems

Supramolecular liquid crystals obtained *via* intermolecular hydrogen bonding have attracted considerable attention during the last

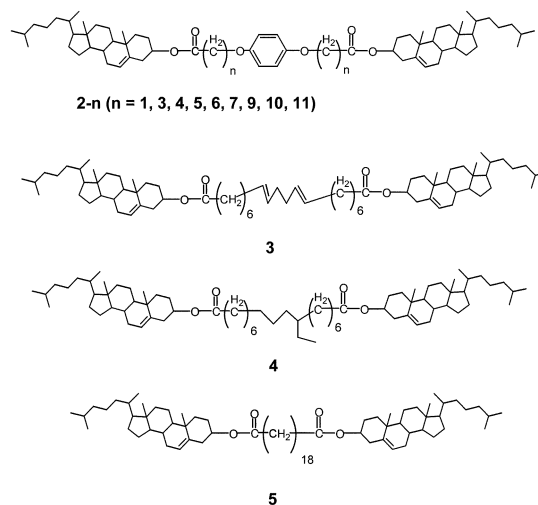


Fig. 8 Structures of symmetric dimesogens.

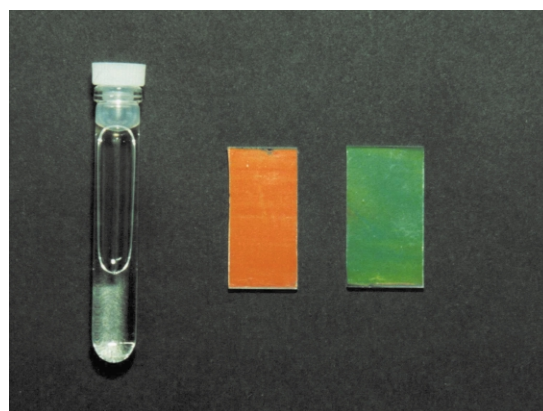


Fig. 9 A photograph taken at room temperature of iridescent green and red solid films on glass plates obtained by spin-coating a solution of **1-8** in dichloromethane at 22–23 and 38–40 °C respectively. (Reproduced from ref. 14 with permission from Wiley-VCH.)

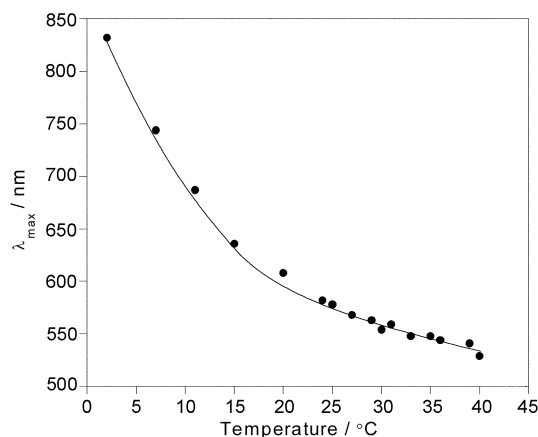


Fig. 10 Relationship between the surface temperatures of the substrate and the wavelength of the transmission band for the colored cholesteric glassy liquid crystalline films obtained from **1-8**. (Reproduced from ref. 14 with permission from Wiley-VCH.)

decade.^{15,16} The prime advantage of hydrogen-bonded mesogens is that their liquid crystalline property can be adjusted easily by changing the hydrogen bond acceptor, hydrogen bond donor or composition percentage. It has been shown that cholesteric glassy liquid crystals can be obtained from hydrogen bonded liquid crystals. Self organization through intermolecular hydrogen bond-

ing between cholesterol derivatives such as cholest-5-en-3 β -yl-4-(pyridin-4-ylazo)phenyl carbonate, cholest-5-en-3 β -yl-3-(4-(pyridin-4-ylazo)phenyl)propyl carbonate and carboxylic acids such as 4-n-alkyloxycinnamic acids, 4-n-butyloxybenzoic acid resulted in the formation of materials showing cholesteric and smectic A phases. Cholesteric glassy liquid crystals showing the characteristic iridescent colors could be obtained by freezing the cholesteric phases of these materials.¹⁷ Cholesterol groups linked to a base like adenine or thymine through a methylene spacer have also been reported to exhibit cholesteric glassy liquid crystalline phase.¹⁸ We have shown that from the hydrogen bonded liquid crystals formed between cholesterol containing hydrogen bond donors and cholesterol containing hydrogen bond acceptors glassy liquid crystalline films maintaining helical molecular order can be generated (**6**; Fig. 11) The relationship between liquid crystalline

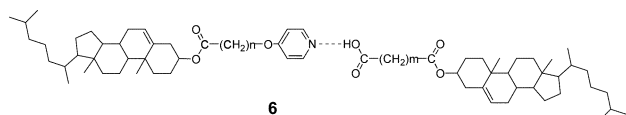


Fig. 11 Structure of hydrogen bonded dimesogens.

properties and alkyl chain length in these hydrogen bonded systems was also reported.¹⁹ In these hydrogen bonded dimesogens different reflection colors of the cholesteric phase were selectively and repeatedly fixed by changing the starting material or rapid cooling. The supramolecular hydrogen bonded complex (**6**, $m = 4$ and $n = 5$) was solidified while maintaining the helical molecular order by rapid cooling from 145 °C to 0 °C. The wavelength of reflection maximum for this glassy liquid crystalline film was found to be 388 nm. Fig. 12 shows the transmission spectra of

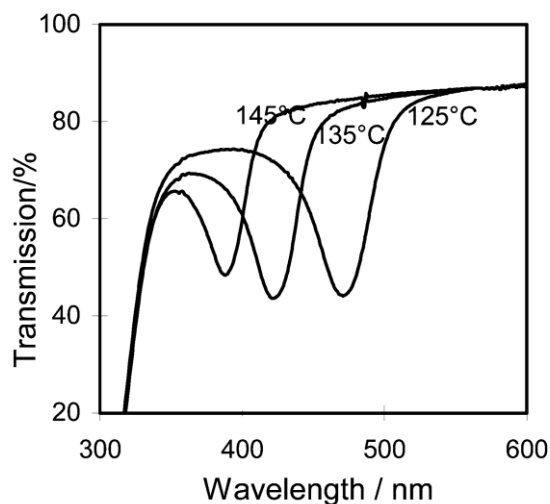


Fig. 12 Transmission spectra obtained for the hydrogen bonded assembly **6** ($m = 4$ and $n = 5$) in colored glassy liquid crystalline state by rapid cooling from different temperatures.

hydrogen bonded assembly **6** ($m = 4$ and $n = 5$) in colored glassy LC state sandwiched between glass plates obtained by rapid cooling from different temperatures. Heating the film at about 60–75 °C can erase the fixed colors in the glassy liquid crystal and the fixation process can be repeated several times. A non symmetric dimesogen built through self assembly *via* intermolecular hydrogen bonding between 3-cholesteryloxy carbonyl pentanoic acid and aromatic mesogen with pyridyl group has been investigated for the incommensurate smectic phases.²⁰

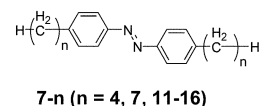
4 Photochemical control of molecular order in dimesogens

In photonics, increasing attention is being paid to the study of molecules or molecular systems whose chemical or physical

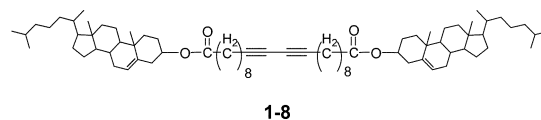
properties can be reversibly controlled using light as a stimulus.^{21–23} Research in this area has been directed towards the development of materials that can respond in a unique manner to the different properties of light such as wavelength, intensity and polarization. Liquid crystalline materials are particularly suited for such applications since their liquid like nature provides the possibility of molecular motion in response to the properties of light. Liquid crystalline materials that can respond to light can potentially have much faster switching times. Such devices can find use in advanced photonic applications such as optical computing and real time holography. In cholesteric liquid crystals the shift in cholesteric pitch induced by a photochemical reaction can be applied to recording materials operating in photon mode. There are two ways of controlling the cholesteric pitch with a photoreaction. First is the case in which the photoreactive compound is doped in the cholesteric liquid crystal, and second the case in which the inherently photoresponsive compound exhibits a cholesteric liquid crystalline phase. From the viewpoint of pitch change due to the modification of chemical compositions in mixed cholesteric liquid crystalline systems, an enormous number of studies have been reported in the literature. Ferguson has reported on the color change of cholesteric phases induced by traces of dissolved gases.²⁴ In the late 1960's, Haas *et al.* reported a change in the selective reflectivity of the cholesteric liquid crystalline mixture composed of cholesteryl bromide and other cholesteryl derivatives on photolysis.²⁵ This change in reflectivity arose from a change in the helical pitch of the cholesteric liquid crystal resulting from the photochemical reaction of cholesteryl bromide in the liquid crystalline mixture. Sackmann has shown that the photoisomerization of azobenzene containing cholesteric liquid crystalline mixtures leads to changes in their reflection wavelength.²⁶ Reversible photoinduced changes in the reflection band have been recently reported in eutectic mixtures of cholesteric liquid crystals containing photoactive moieties, chiral photoactive molecules dissolved in the nematic LCs and in the photoresponsive polymeric systems.²⁷

4.1 Dimesogens doped with photoactive molecules

To control the optical properties of glass forming dimesogens by light, azobenzene derivatives have been doped.^{28,29} Fig. 13 show



7-n ($n = 4, 7, 11-16$)



1-8

Fig. 13 Structures of azobenzene dopants and cholesteric liquid crystalline host.

the structures of azobenzene derivatives used in the experiments on photochemical control and fixation of cholesteric pitch. These azobenzene derivatives exhibit fast thermal isomerization from the *cis* state to the *trans* state under the experimental conditions (120 °C) and show good miscibility in dicholesteryl esters. A red reflection band has been observed for the mixture **1-8** and **7-12** (98:2 weight ratio) combined between two quartz plates (about 10 μ m thickness) at 120 °C (cooling cycle). This mixture was irradiated with 366 nm UV light, keeping it at the cholesteric temperature. Upon irradiation, the color of the thin film changed from red to blue passing through green due to the *trans-cis* isomerization of the azobenzene group. The thin film solidified retaining the iridescent color shown in the normal cholesteric phase, upon rapid cooling to 0 °C. Different colors can be fixed by changing the energy of the irradiated UV light because of the formation of different *cis:trans* ratios of the photoactive moiety.

Fig. 14 shows a cholesteric glassy liquid crystalline film with images obtained by the photochemical mode. In the glassy liquid

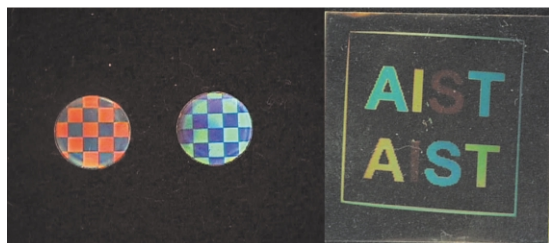


Fig. 14 Photographs of the cholesteric glassy liquid crystalline films recorded using a photochemical mode. (Reproduced from ref. 28 with permission from Wiley-VCH.)

crystalline film obtained after irradiation, *cis*-azobenzene thermally reverts back to the *trans*-state without inducing any shift in the reflection band. Due to the rigidity of the glassy liquid crystalline matrix, the molecular alignment would not be disturbed by the reverse *cis* to *trans* isomerization process. The shift in the wavelength from that of pure dicholesteryl mesogen doping with the azobenzene derivatives depends on the length of the alkyl chains on the azobenzene. The dependence of the cholesteric pitch on the alkyl chain length and temperature observed would be caused by the difference in the interaction between each azobenzene and the host cholesteric liquid crystal. It is because the macroscopic chirality of cholesteric liquid crystals is induced by the microscopic chirality of the constituent molecules. Change in the pitch length of cholesteric helix on temperature variations can be explained as the associated change in the orientational parameter of the molecule or because of smectic cybotactic groups (smectic fluctuations). Reports on cholesteryl nonanoate and myristate which contain a pretransition smectic state show smectic domains

in the cholesteric liquid crystalline phase near the cholesteric to smectic transition temperature.³⁰ There are also a few reports on chiral polymeric systems which show smectic fluctuations in the cholesteric liquid crystalline phase.³¹ We employed a variety of dialkyl compounds as solutes including azobenzene, azoxybenzene, biphenyl, binaphthyl, benzene, *etc.*, as shown in Fig. 15, and investigated the correlation of the helical pitch with the structure of molecules added to the cholesteric liquid crystals.³² These results lead to the conclusion that the dopants with a mesogenic core and the proper length of alkyl chains induce an anomalous increase in the helical pitch of the cholesterics through the induction of smectic clusters (Fig. 16).

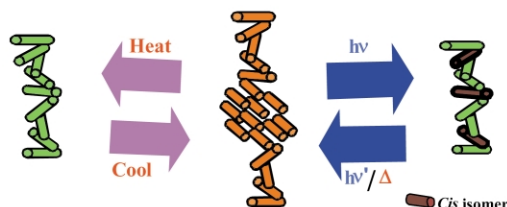


Fig. 16 Schematic representation of the change in the pitch length of a cholesteric liquid crystal by smectic fluctuations in the thermal and photo mode.

In the doped system consisting of chiral dimesogen and alkyl azobenzenes it was found that thermal stability of the glassy state of the dimesogen is decreased by an increase in the content of the dialkyl azobenzene. To solve this problem of destabilization of the glassy liquid crystalline state of the mixture, new dimesogens containing azobenzene and cholesterol moieties, **17a–17e**, have been synthesized (Fig. 17).³³ The effect of the doping on the reflection band depended significantly on the length of the alkyl chain on the azobenzene group of the dopant, maximizing at the

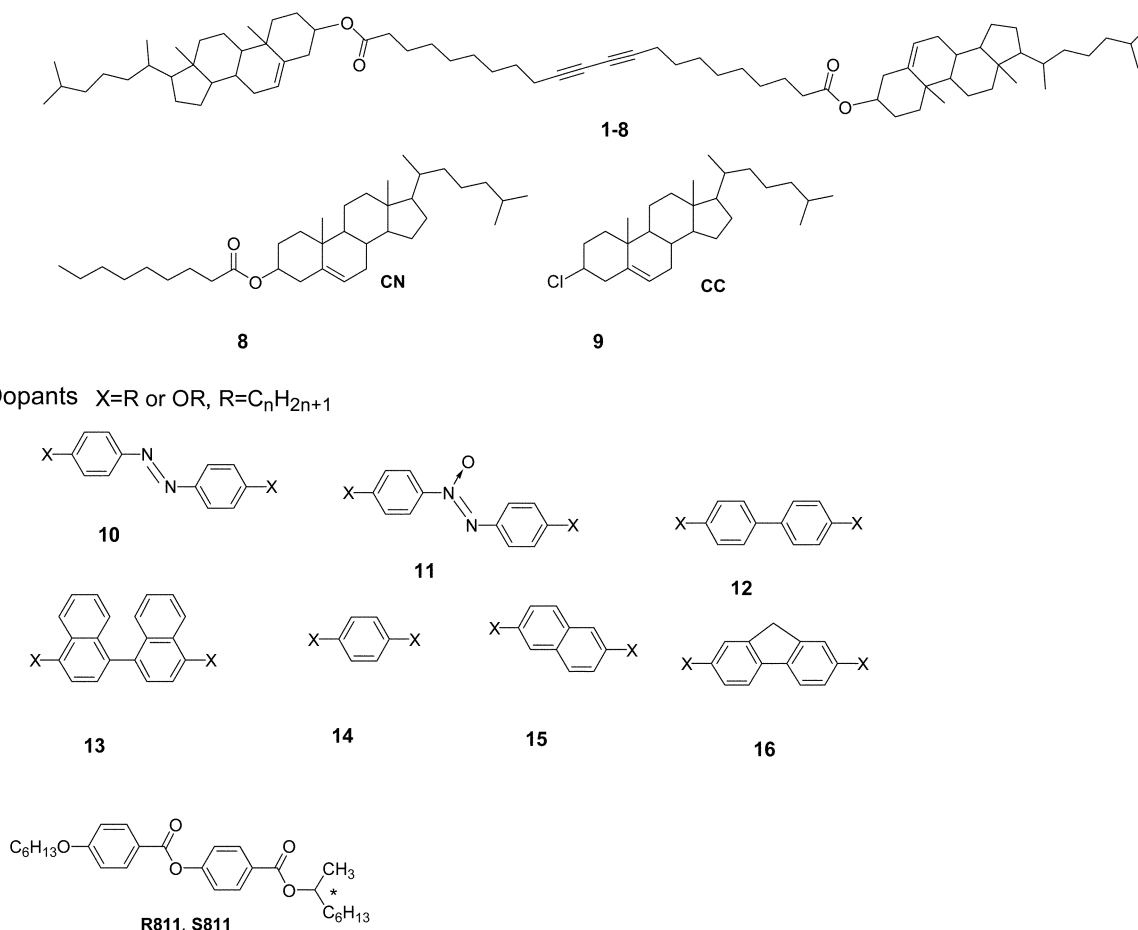


Fig. 15 Structures of cholesteric hosts and dopants.

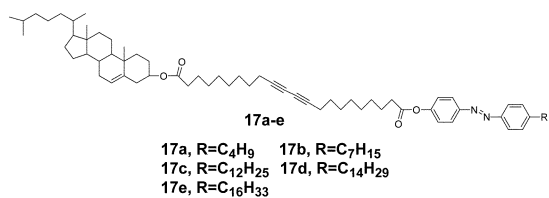


Fig. 17 Structures of unsymmetric photoresponsive dimesogens.

heptyl group. The thermal stability of the glassy state maintaining the cholesteric color of the dicholesteryl compound was found to be higher with the photoresponsive dopant having a cholesteryl group rather than dialkyl azobenzene.

4.2 Inherently photoresponsive dimesogens

In this study, photochromic and glass forming liquid crystalline compounds consisting of a cholesteryl group and an azobenzene moiety connected with a long flexible aliphatic spacer, were examined.^{33–35} Compound **17** only exhibited a smectic phase but some of compounds **19–n** (Fig. 18) show cholesteric liquid

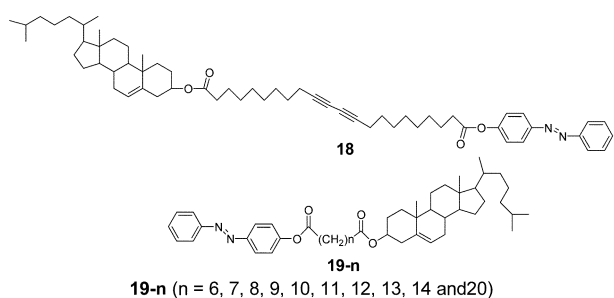


Fig. 18 Structures of unsymmetric photoresponsive dimesogens.

crystalline properties. Upon irradiation at 366 nm, which induced *cis-trans* isomerization of the azobenzene units the reflected wavelength shifted to a shorter wavelength during the early stage of the irradiation. Further irradiation induced a phase transition to isotropic. Under 436 nm light at 65 °C, the reflection band of compound **18** gradually shifted from 570 to 480 nm, but a phase transition to isotropic is not observed, even at the photostationary state. Similarly the reflection band of compound **19–20** shifted from 558 to 470 nm at 85 °C under 436 nm wavelength. Different results in these compounds depending on the exposure wavelength can be explained by considering the concentration and the concentration distribution of each isomer in the film after irradiation. The cholesteric reflection of the irradiated samples could be able to fix in the glassy liquid crystalline state. To get more information about the length of the linker in the dimesogen and the reflected wavelength and fixation properties, dimesogenic compounds linked by an alkyl chain whose length varied from C₆ to C₁₄ (**19–n**) were prepared. Cholesterol–azobenzenes linked with an alkyl chain spacer showed odd–even effects in their reflection wavelength as a function of spacer length. Compounds with even number of methylene units showed a drastic change in their reflection wavelength (102–225 nm) on temperature change compared to their odd counter parts (9–14 nm). UV photolysis using a 366 nm wavelength of the cholesteric super cooled state resulted in a hypsochromic shift in the reflection wavelength. For the dimesogen with an alkyl chain length of 8 (**19–8**), photolysis at 366 nm caused a shift of the maximum reflected wavelength from 684 to 553 nm (at 100 °C, cooling cycle, Fig. 19). A maximum wavelength shift of 215 nm (703–488 nm) has been observed for the dimesogen having a 12-methylene spacer (**19–12**) on photolysis at 80 °C (cooling cycle). By rapid cooling of the compounds from the cholesteric temperature to 0 °C, glassy liquid crystalline films maintaining helical molecular order were obtained. Change in the reflection wavelength with temperature in these materials could be explained by considering the formation of smectic fluctuations. Fig. 20 shows

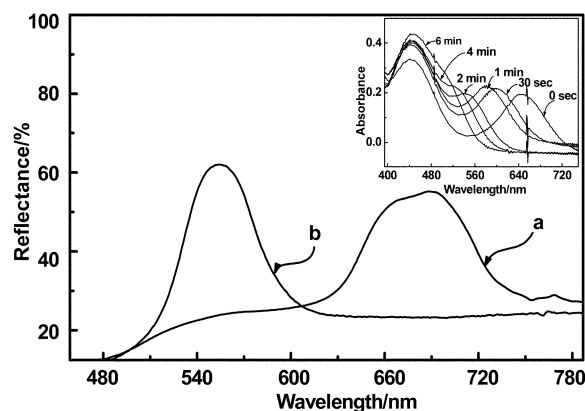


Fig. 19 Reflection spectra of **19–8** at 100 °C (cooling cycle) using 366 nm wavelength at different time intervals: a, 0 min; b, 6 min. Inset shows the absorption spectra of **19–8** under similar conditions.

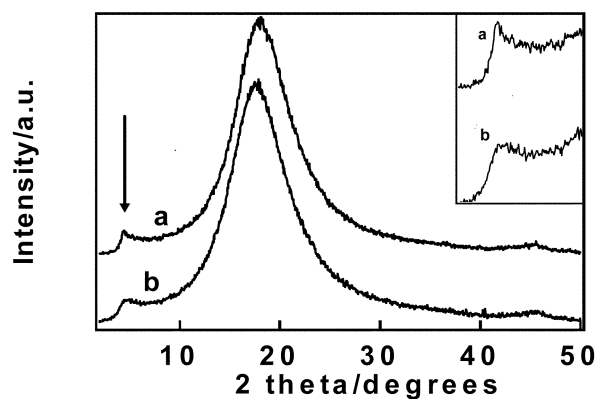


Fig. 20 The intensity profiles of the X-ray diffraction pattern exhibited by **19–10** at different temperatures measured in the cooling cycle: a, 85 °C and b, 125 °C. Inset shows the expanded scale from 3 to 15 degrees.

the X-ray diffractograms obtained for **19–10** at 125 °C and 85 °C measured in the cooling cycle. The diffraction pattern of **19–10** at 125 °C shows two broad peaks, at 5.06 Å and 19.68 Å. The peak at 5.06 Å is due to the lateral liquid like correlation of the molecules within the layers and the peak at 19.68 Å is because of smectic fluctuations. As the cholesteric phase is cooled to 85 °C the smectic fluctuations becomes more pronounced leading to a sharpening of the low angled peak (19.68 Å) (Fig. 20a). A similar trend was observed in the dimesogens containing even number of methylene units ($n = 6, 8, 10, 12$ and 14).

4.3 Photochemical phase transitions in dimesogens

Phase transition can be triggered by photochemical reactions of guest molecules doped in the liquid crystal matrices. There have been several reports on such photoinduced phase transitions of liquid crystals containing guest molecules such as azobenzene and spiropyran derivatives.³⁶ In liquid crystals containing azobenzene derivatives, the rod like shape of the *trans* form of the azobenzenes tends to stabilize the LC phase while the *cis* form tends to destabilize it. Thus, *trans-cis* photoisomerization of the azobenzene derivatives can lead to lowering of the LC to the isotropic (I) phase transition temperature of the mixture. Time-resolved studies using lasers have shown that light induced phase transition in such systems usually occurs in the time scale of 200–500 ms, although the photochemical transformation of the guest molecule is usually complete within the laser pulse duration (< 10 ns). These studies indicate that the response of the LC host material to photochemical transformation of the guest is very slow.

The compounds shown in Fig. 17, **17–n** exhibit smectic A liquid crystalline phase. These compounds were irradiated by 366 nm light at their liquid crystalline temperatures. Phase transition from the birefringent liquid crystalline to the isotropic phase occurred,

which is observed using an optical microscope with cross polarizers (Fig. 21). In the dark the azo-group thermally isomerizes from *cis*

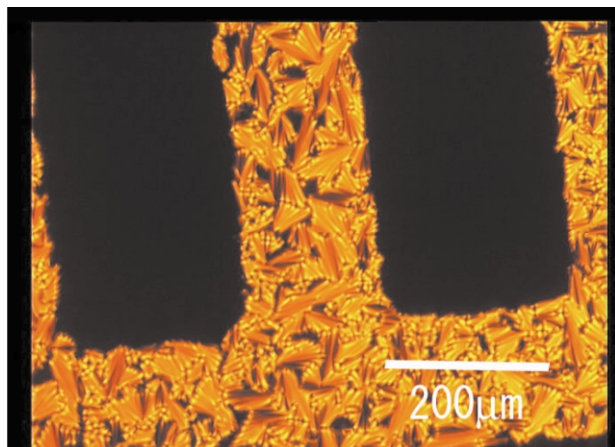


Fig. 21 Optical textures of the compound **17c** at 98 °C observed after the UV irradiation at 366 nm through a photomask with transparent lines of 200 μm width after the irradiation. (Reproduced from ref. 33 with permission from the American Chemical Society.)

to *trans* and the compounds return to the original liquid crystalline states. Furthermore the molecular alignment of these compounds at their liquid crystalline temperatures before and after irradiation was fixed in the glassy state by rapid cooling to 0 °C. The glassy state obtained by cooling was stable at room temperature for all compounds, and no effects in the molecular alignment were observed, even after UV irradiation in the glassy state. Upon heating to its isotropic temperature, the glass was completely melted. If film samples of **17a–e** between thin glass plates are irradiated with 366 nm wavelength through a photomask at a temperature around 2 °C below the isotropic–smectic transition and rapidly cooled, a pattern with dark and light areas corresponding to the isotropic and smectic parts is obtained (Fig. 22). A smectic to

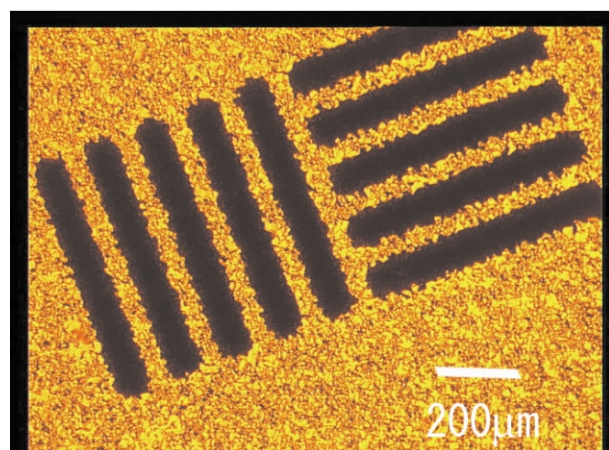


Fig. 22 Optical textures of the compound **17c** at room temperature observed after UV irradiation through a photomask with transparent lines at 98 °C followed by quenching. (Reproduced from ref. 33 with permission from the American Chemical Society.)

cholesteric photoinduced phase change was observed in the case of dimesogen **20** (Fig 23).³⁷ Thin layers of the dimesogen **20** were sandwiched between cover slips containing 10 μm glass spacers and the film was heated to the isotropic state and slowly cooled to 100 °C. At this temperature the film showed the focal conic fan shaped texture characteristic of smectic A phase. On irradiation for 30 seconds with light from a 500 W medium pressure mercury lamp filtered through a 366 nm filter the film turned cholesteric, which was confirmed from the presence of a selective violet reflection and the cholesteric texture. Photolysis of *trans*-**20** would lead to partial isomerization to its *cis* form. Cholesteric to isotropic phase

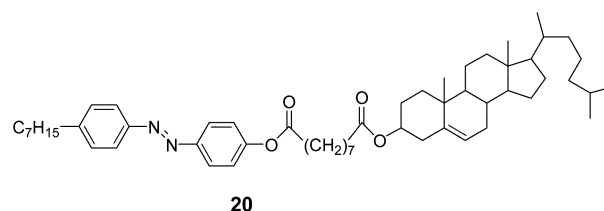


Fig. 23 Structure of unsymmetric photoresponsive dimesogen.

transition was observed upon continuous photolysis of the thin film of **20**, because conversion from *trans* to the *cis* isomer leads to the destabilization of the LC phase due to its bent structure. On keeping the irradiated isotropic film of **20** at same temperature (100 °C), *cis* to *trans* reversal of the dimesogen **20** occurred, which changed the phase to cholesteric and further to smectic A. Fig. 24 show the

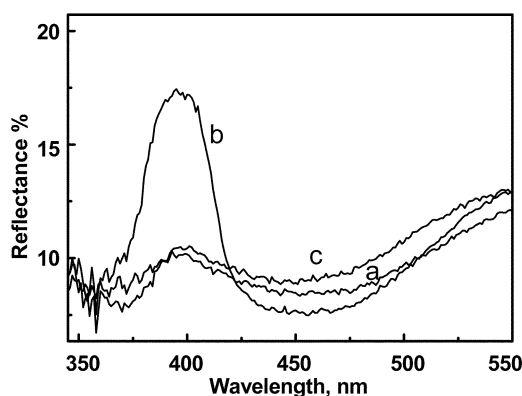


Fig. 24 Reflection spectra of **20** at 100 °C (Cooling): a) before photolysis, SmA phase; b) after photolysis for 30 s using 366 nm light; c) smA phase regenerated after the thermal *cis*–*trans* reversal. (Reproduced from ref. 37 with permission from the American Chemical Society.)

reflection spectra obtained for **20** at 100 °C before and after photolysis studies. After photolysis for 30 seconds, a reflection band of 394 nm was observed, which was red shifted to 415 nm suggesting partial thermal reversal of *cis* **20** back to its *trans* form. On keeping the film at same temperature for 60 seconds following irradiation, the SmA phase was completely regenerated. The entire process can be schematically represented as shown in Fig. 25.

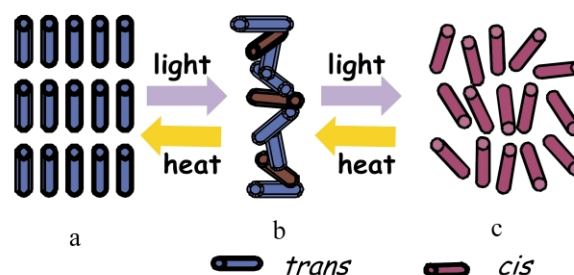
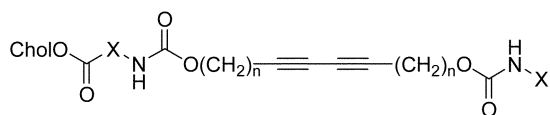


Fig. 25 Schematic representation of the photochemical switching process in **20**. (Reproduced from ref. 37 with permission from the American Chemical Society.)

5 Dimesogens forming photoresponsive organo gels

To study the interaction between chemical structures and supramolecular organization we introduced urethane units in the dimesogen containing dicholesteryl ester groups (Fig. 26).^{38,39} Urethane units in the compounds can form intermolecular hydrogen bonds between neighbouring molecules which can stabilize the one dimensional molecular organization of the gel as shown in Fig. 27. These compounds exhibits gel state in non-polar solvents such as cyclohexane or mixtures of hexane and dichloromethane. The gel



- 21a: $n=1$, $\text{X}=(\text{CH}_2)_2$
 21b: $n=1$, $\text{X}=(\text{CH}_2)_3$
 22a: $n=2$, $\text{X}=\text{CH}_2$
 22b: $n=2$, $\text{X}=(\text{CH}_2)_3$
 23a: $n=3$, $\text{X}=\text{CH}_2$
 23b: $n=3$, $\text{X}=(\text{CH}_2)_2$
 23c: $n=3$, $\text{X}=(\text{CH}_2)_3$
 23d: $n=3$, $\text{X}=\text{CHCH}_3$ (L-Ala)
 23e: $n=3$, $\text{X}=\text{CHCH}_3$ (D-Ala)
 24a: $n=4$, $\text{X}=\text{CH}_2$
 24b: $n=4$, $\text{X}=(\text{CH}_2)_2$
 24c: $n=4$, $\text{X}=(\text{CH}_2)_3$
 24d: $n=4$, $\text{X}=\text{CHCH}_3$ (L-Ala)
 24e: $n=4$, $\text{X}=\text{CHCH}_3$ (D-Ala)
 24f: $n=4$, $\text{X}=\text{CHCH}_2\text{CH}(\text{CH}_3)_2$ (L-Leu)

Fig. 26 Structures of gel forming dimesogens.

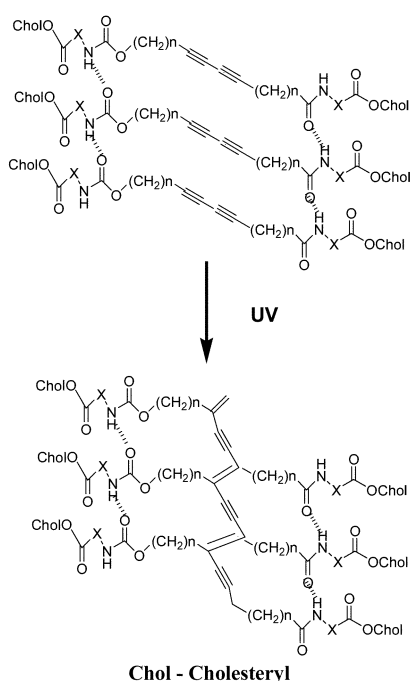


Fig. 27 Schematic representation of light induced polymerization in the gel state.

formed with the mixtures of hexane and dichloromethane were transparent, while those with cyclohexane were slightly turbid. Most of the gels polymerize on UV irradiation and change their color from colorless to dark blue, purple, red, pink, and orange. The color depends on the conjugation length of π electron of polydiacetylene. Fig. 28 shows photographs of the cyclohexane gel of compound **24a** before and after irradiation. The absorption spectra exhibit bands at 630 and 582 nm after photoirradiation. This can be attributed to the exciton band of polydiacetylene. Photopolymerization increased the stability of the gel state. The T_{gel} for cyclohexane was 45 °C before polymerization. The polymerized gel maintained its shape when heated to the boiling point of cyclohexane. Gelation and photopolymerization studies were extended to the various alkyl linkers connecting the cholesteryl groups, urethane and diyne units. Fig. 29 shows Energy Filtering Transmission Electron Microscopy (EF-TEM) pictures of **23b** before and after photopolymerization. It can be concluded that intermolecular hydrogen bonding between urethane groups on both sides of the diyne group in these gelators makes the gel state stable and the distance between diyne groups and the angle between the diacetylene rod and the stacking axis in the gel state preferable for

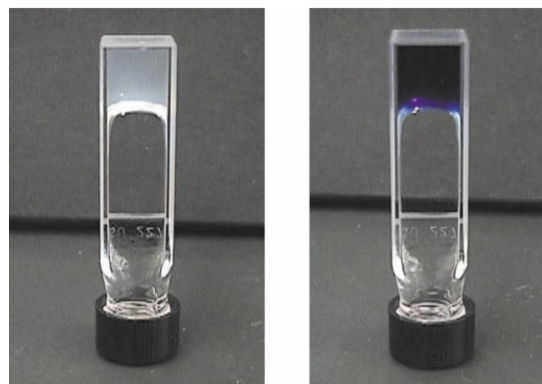


Fig. 28 Photographs of cyclohexane gel of **24a** before (left) and after (right) photoirradiation for 1 min. (Reproduced from ref. 38 with permission from the American Chemical Society.)

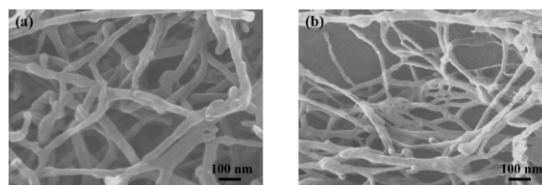


Fig. 29 EF-TEM pictures of cyclohexane gel containing **23b**; a) un-irradiated, b) irradiated.

the 1,4-addition reaction resulting in the formation of colored nanofiber materials.

This method is a new strategy of making nanofibers using bottom-up approach. Conjugated polymers with nanostructures has lot of advantages in the optics as well as electronics. In the present method one dimensional gel structure helps the monomeric molecules to oriented to give 1–4 addition and obtaining nano-structured materials.

6 Conclusions

The entire work presented in this review can be summarized as how weak bonding such as van der Waals forces or hydrogen bonding facilitates molecules to form molecular organizations, which perform suitable functions in photonics or information technology. Properties of dimesogenic materials having at least one cholesteryl moiety have been discussed. Some of the compounds exhibit not only liquid crystalline phases but also glass forming properties analogous to the polymeric components. By rapid cooling of these compounds from their cholesteric temperature to 0 °C, cholesteric glassy liquid crystalline films maintaining helical molecular order can be obtained. Different reflection colors of the cholesteric phase were selectively and repeatedly fixed by changing the starting temperature of rapid cooling. Because of the low molecular weight the realignment of molecules in their liquid crystalline state is fast and it is possible to control their super helical structure by the addition of photoactive dopants within 10 seconds. These features of the dimesogens could be used in dynamic and static optical applications. This article also describes various possibilities for obtaining dimesogens with specific functions: first dimesogens with dicholesteryl groups and second materials which have one azobenzene moiety and a cholesteryl group. Two mesogenic units can be attached by covalent bonds or *via* intermolecular hydrogen bonding interaction between suitable hydrogen bond donors and acceptors. In the case of dimesogens in which one of the mesogenic units is photoresponsive such as azobenzene, these compounds detect the incident light by themselves and induce photochemical phase transitions depending on the amount of light or generated *cis* isomers. By incorporating urethane units into dimesogens containing dicholesteryl esters, intermolecular hydrogen bonding between the molecules is introduced and the compound could gelate in

organic solvents by forming stable nanofibers of conjugated polymer after photoirradiation.

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