Light responsive liquid crystal soft matters: structures, properties, and applications

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ABSTRACT
Stimuli-responsive soft matters have been recognised by many scientists and engineers as very important because of their inherent characteristics in response to environmental changes. In particular, there has been much progress over the last few years on light-responsive soft matters that can respond remotely. By controlling the packing behaviours and the physical properties of the photosensitive liquid crystal (LC) molecules, the application field is expanding, including the use in flexible polarisers, patterned objects, logic devices, biomimetic photonic crystals and energy harvesting materials. This review discusses the general concept of azobenzene-based LC compounds from small molecules to macromolecules and their corresponding structural evolutions in solid states. Finally, we identify the challenges faced in the research of photoresponsive organic materials and present future applications.

1. Introduction

Over the years, researches on liquid crystals (LCs) have made significant advances in understanding the self-assembly behaviour of soft materials [1]. The LC state is a unique combination of molecular mobility and orientational order at the intermediate phase between solids and liquids [2]. Generally, a thermotropic LC (TLC) consists of two components, rigid core and flexible chain [3]. Based on the shape of the core, TLC is classified as conventional and nonconventional LC [4]. The former includes calamitic and discotic molecules, while the latter contains a wide range of anisotropic mesogens such as polycatenars, bent cores and star-shaped molecules [5]. They often form nematic, smectic, cholesteric, hexatic, and blue phases depending on the temperature [6]. For a lyotropic LC (LLC) comprising fluidic molecular complexes, it is commonly formed by the self-organisation of amphiphilic molecules in organic or inorganic solvents [7]. LLC molecules with a hydrophilic head and hydrophobic tail form the superstructures of micelles, vesicles and microtubules [8].

Control of the ordered structure of LC molecules is attractive for building well-organised systems with desired properties [9]. Commercialisation of an LC display (LCD) is a good example [10]. This is the result of the truly interdisciplinary effort of the scientific community [11]. In order to achieve excellent optical quality, the LCD requires a lot of materials such as light sources, polariser films and colour filters. The LC is present between the encapsulated glass substrates [12]. To control information visualised by polarised light, LC molecules are uniformly aligned over the display panel with the help of alignment layers [13]. Recently, most mobile LCDs have been transformed into touch-sensitive and haptic functions [14]. Along this line, it is important to select the proper alignment of the LC [15]. The LC director should not show any touch traces following pooling and bruising [16]. Therefore, it is important to understand the structure and property relationships in the LC field and to translate scientific knowledge into practical applications [17].

Self-assembly of the LC follows the basic principle of soft materials by minimising the excluded volume [18]. Additionally, maximisation of the interaction energy through van der Waals, charge transfer, metal coordination, polar, ionic, and hydrogen bonding also contributes to the formation of LC mesophases [19]. If the LC can be prepared by chemically or physically connecting the photochromic group, these photochromic LC molecules can be applied to the remotely controllable materials [20]. The azobenzene chromophore can be transformed between two isomers with different absorption spectra induced by photoirradiation [21]. Thus, photoisomerisation from trans-to-cis and cis-to-trans of the azobenzene leads to changes in the electronic as well as the...
geometrical structure of the molecules [22]. The choice of wavelength, intensity, and polarisation of light can affect greater degrees of control in the light-induced phase transformations of azobenzene-based LC molecules [23]. However, a photoresponsive behaviour of the soft materials is reversible or irreversible, depending on the packing symmetry of the chromophores, especially in the solid state [24].

In this introduction, we briefly outline the remote-controllable LC phase from the fundamental principle and application point of view. In section 2, the nature of photochemical isomers of azobenzene molecules is discussed. Section 3 describes the concept of the self-assembly behaviour of photoresponsive LC molecules doped into the LC medium. It also provides anisotropic behaviour with practical application. The orientational order of the chromophore in the molecules is critical in determining the photochemical reaction, and building a profound knowledge of these correlations is essential for both the synthesis of materials and the amplification of physical properties. Finally, conclusions and outlooks on the subject are provided.

2. Principles of photocontrol

The chromophoric compound is a good candidate for molecular photoswitch that can interconvert between two or more forms [25]. The isomerisation is triggered by a certain wavelength of light [26]. The most common dyes are classified as azobenzene and stilbene derivatives that can form the trans and cis state, or as diarylethene and spiropan moieties that can show open and closed state [27]. Among them, azobenzenes are by far the most extensively used chromophore because of their easy syntheses, high quantum yields, and fast responses [28]. It is recognised from early on as a suitable photochromic molecule to influence not only the polarity but also the structure within the materials upon light irradiation in a reversible manner [29]. The azobenzene in trans state is a planar molecule with zero dipole moment (Figure 1a) [30]. The thermodynamically stable trans conformer of azobenzene can transform to its metastable cis conformer exhibiting a kink molecular shape [31]. As shown in Figure 1b, the absorption spectra indicate that azobenzene reaches into a new photostationary state when the 365 nm ultraviolet (UV) light is irradiated. The absorption band between two isosbestic points is originated from the trans form of azobenzene. The ground state of the cis conformer of azobenzene is excited to the π* state by absorbing the UV. While the visible (Vis) light is exposed, the amount of trans conformational azobenzene is increased again (Figure 1c). Equilibrium states between two photostationary transitions are fully reversible process, which can allow us to fabricate photoresponsive materials. The inclusion of azobenzene into functional materials is the widely used approach towards photomodulation of ordered structures. In this method, the azobenzene is chemically connected to small molecules, macromolecules, and supramolecules.

3. Remote controllable ordered phases

Depending on the irradiation wavelength, the azobenzene shows the fascinating property to undergo photoisomerisation from trans to cis, and vice versa [32]. Due to their optically anisotropic nature, the trans azobenzenes have intense absorption along the long axis [33]. It makes them an ideal dichroic compound [34]. Since the absorption of incident light from the dye molecule with its polarisation parallel is usually more than that with perpendicular polarisation, azobenzene-based dyes have often been used as dichroic mesogens for tuning polarised light [35]. The performance of the electro-optical device like host-guest liquid crystal (LC) display closely depends on the chemical structures of

![Figure 1. Chemical structures of two isomerised states of azobenzene molecules (a). Absorption spectra changes of azobenzene-based supramolecules upon irradiation of UV (b) and Vis (c) light, respectively. Reproduced with permission [30].](image-url)
doped dyes in LC media [36]. To obtain a sufficiently large dichroic ratio (DR), we synthesised a palladium(II)-extended dichroic mesogen abbreviated as AZ₄Pd (Figure 2a) [37]. The organometallic complex through a pyridine moiety in the defined manner enables to increase the molecular length of the dichroic mesogen.

The light polarisation is mainly determined by the molecular orientation. To figure out a preliminary study on the polarised absorption property, a mixture of 1.0 wt% guest AZ₄Pd dye and 99.0 wt% host nematic (N) LC is capillary-filled into the indium-tin-oxide (ITO) cell coated with anti-parallel rubbed polyimide alignment layer. As shown in Figure 2b, it is realised that the absorption intensity of AZ₄Pd at the parallel direction (A₀) along the polariser is 14.6 times higher than that at the perpendicular direction (A₉₀), that equals 14.6 at absorption maximum (λ = 365 nm). A high order parameter (S = 0.82) and DR = 6.21 support that AZ₄Pd molecules are uniaxially oriented along the LC molecule. The polarised absorbance can be switched by alternating the wavelength of the irradiated light. At the initial state, the obvious dichroic feature is fully identified in the polar plot with the absorption maximum of 365 nm at θ = 0° and 180° (Figure 2c). After UV light irradiation, the absorption intensity of the A₀ and A₉₀ from the optical cell is 2.87 and 2.61, respectively. Along this line, DR in the metastable cis state is decreased to 1.09. As a result of the photochemical reaction, the AZ₄Pd molecule in the metastable state destabilises the ordered phase (S = 0.03). The transition moment of AZ₄Pd is quite arbitrary, and thus the anisotropic property is totally lost. When the Vis light is irradiated, the polarised absorbance returns back to the initial highly ordered state. Both DR and S values are reproducible in successive measurements. It is worth mentioning the fact that the guest AZ₄Pd molecules are not phase separated out from the host LC medium due to the internal free volumes between two alkoxy chains that can improve the compatibility of the guest dye with the LC medium.

By utilising the light as external stimuli, the molecular orientation of soft materials showing the N phase can be controlled [38]. Here, we attempt to modulate the chiral nematic (N*) LC which is a chiral version of N phase possessing solely 1D orientational order along the long axis of LC molecules [39]. Because the N* phase has the helical superstructure, it exhibits optically active variants [40]. Typically, the selective reflection colours of N* phase depend on the periodicity of the helical pitch (P) and the refractive index of the system [41]. Therefore, the N* films have been considering applications for the colour switchable materials [42]. As shown in Figure 3a, a photochromic chiral molecule (AZ₂BP) was synthesised by introducing the azobenzene chromophore to the chiral naphthyl...
group with (R)-configuration [43]. The N* phase is readily formed by doping the 1 wt% of AZ₂BP into the achiral LC medium. The aligned N* texture is observed at room temperature under polarised optical microscopy (POM). A characteristic texture of oily-streak form is observed for the N* mesophase (Figure 3b). By adjusting the concentration of AZ₂BP, the length of P is optimised to reflect the light in the visible wavelength region. At the initial state, as shown in Figure 3c, the optical cell shows blue colour with reflection band at around 480 nm. Upon irradiating at UV light, the reflection colour shifts to green (545 nm) within 5 s. The prolonged illumination of UV light further drives the reflection band towards longer wavelengths. At the given condition, the spectral change reaches the equilibrium state within 10 s and eventually, the reflection saturates in red (620 nm). This colour change is due to photoisomerisation of the AZ₂BP. As a result of trans to cis isomerisation, a helical twisting power (HTP) of the chiral dopant is decreased. The subsequent lengthening of P results in a continuous red shift of reflection spectra as a function of irradiation time. In the absence of UV light, the reflection colour gradually shifts to the short wavelength region and restores its original blue colour within 20 s. The results indicate that the photoisomerisation of chiral dopants of AZ₂BP reversibly manipulates the selective reflection of light of N* film. In addition, the broadening of reflection bands can be understood by the intensity-dependent isomerisation. The UV light intensity exponentially decays as the path length increases along the optical cell thickness direction because the azobenzene chromophore strongly absorbs the UV light. Therefore, the population of cis isomer with a lower HTP is higher near the top side of the optical cell, compared to the bottom side. The gradient of the photostationary state creates the P distribution.

Since the light-driven phase structure changes in the bulk states rely on their molecular packing symmetry, understanding the self-assembly features of the functional photoresponsive material is significantly important [44]. Note that the photochemical isomerisation is basically suppressed in the highly ordered phases owing to the lack of free volume [45]. However, this reaction can be allowed in the partially ordered mesophases [46]. Therefore, the fine control of intermolecular interactions between the programmed molecular building blocks by light is interesting to obtain the desired properties of the soft materials [47]. The strategy of the molecular design for AZ₂CT is the self-assembly of an amphiphilic molecule into the highly ordered crystalline (K) and the low-ordered LC phase [48]. The polar head group of carboxylic acid function enhances the supramolecular aggregates via the intermolecular hydrogen bonding. The hydrophobic and rigid diacetylene chains tend to induce the nanophase separation in the intramolecular level (Figure 4a). Based on the careful investigation with thermal, microscopic, and scattering techniques, it is realised that the AZ₂CT molecules basically form the layer structure. As shown in Figure 4b, a pair of diffraction peak at 2θ = 2.05° on the meridian is observed by irradiating X-ray normal to the shear direction (SD) of the macroscopically oriented AZ₂CT sample at 100°C (Figure 4b). The q-value ratio of 1:2:3 is detected in the low angle region indicating the formation of smectic (Sm) domain with 8.61 nm periodicity. At lower temperatures, the K phase is found with the monoclinic lattice parameters of a = 0.61 nm, b = 0.90 nm, c = 9.74 nm and α = γ = 90° and β = 60°.

The reversible photoisomerisation properties of azobenzene can be applied for the light modulating devices. To realise the optically tunable thin films, the efficient photochemical processes of the AZ₂CT
compound should have occurred in the solid state. However, the microphotograph and diffraction patterns of AZ\textsubscript{1}CT in the K phase are not changed even after the UV light irradiation. This result indicates that the photo-induced isothermal phase transition does not take place in the K phase because of the laterally close-packed molecules within the layers. As shown in the POM images of Figure 4c, the Sm phase is transformed into the disordered isotropic (Iso) liquidus state under the UV light exposure. This photoinduced isothermal phase transition is also monitored by wide-angle X-ray diffraction (WAXD) experiments. A weak amorphous halo has suddenly appeared with the disappearance of reflection peaks on the meridian. The Sm layer is totally collapsed by dissociation of the long-range order, which is triggered by the increased population of the metastable cis isomer. As expected, the SmA phase is recovered with the same layer periodicity when the UV light is blocked (inset of Figure 4d). From these results, the history of molecular orientation can be manipulated during the photochemical isomerisation of the AZ\textsubscript{1}CT in the ordered phase (Figure 4e).

The control of molecular alignment is one of the important technologies for high-performance optical devices [49]. Particularly in the LCD industries, the orientation of anisotropic molecules has been achieved by rubbing the polymer-based film [50]. The polyimides have been widely used because they exhibit strong anchoring interactions with the LC molecules and mechanical stability onto the substrates [51]. However, the mechanical contact methods often generate residual stresses and dust particles resulting in deterioration of electrical and optical performances of the LCD [52]. A contact-free alignment method such as photoalignment has been intensively investigated [53]. Modification of LC anchoring conditions of the surfaces can be achieved by forming the monolayer on the top of the substrates with photochromic materials exhibiting photoisomerisation, photodimerisation, photopolymerisation, and photodecomposition [54]. Transforming the azobenzene chromophores between trans and cis form has
some advantages [55]. Overall LC orientations are easily controlled to obtain reversible planar (PA, LC director is parallel to the surface) and vertical (VA, LC director is perpendicular to the surface) LC alignment [56]. In order to modify the surface in the LC doped optical cell, a series of photoresponsive giant surfactants (AZₙCE, where n = 1 and 3) containing both photochromic azobenzene mesogens and carbohydrate head group was prepared [57].

The LC mixtures with contents of 0.1 wt% AZₙCE are prepared by using a vortex mixer. The test optical cells with 10 μm cell gap are fabricated by sandwiching the two ITO glass substrates. The LC and AZₙCE mixtures are filled into the optical cells on a 120°C, which can avoid the flow effect of anisotropic molecules. At room temperature, uniform giant surfactants monolayers are constructed by the phase separation. The AZ₁CE diffused onto the substrates and self-assembled to the expanded monolayer structure. On the other hand, the AZ₂CE formed the condensed monolayer structure on the substrates (Figure 5a). As shown in Figure 5b, topological observation determined by atomic force microscopy (AFM) indicates that the 0.1 wt% AZ₁CE coated surface exhibits many protrusions. It makes enough empty spaces for the LC molecules to partly penetrate into the expanded structure for the construction of the VA layer. The height profile of the 0.1 wt% AZ₂CE is almost identical to that of the AZ₁CE coated surface (Figure 5c). However, it results in the PA rather than the VA, because the LC molecules cannot crawl into the condensed structure. It is interesting to note that the orientational order of the LC is transformed from VA to PA by irradiating the AZ₁CE film with the 365 nm light. The azobenzene in the cis state of the AZ₁CE monolayer closes the empty space of the protrusion for LC molecules to crawl.

Organised structures of the LC molecules trapped inside the 3D networks are considered as substantially dilute crosslinked systems [58]. Due to the physical bonds, it does not exhibit any characteristic signal of flow in the steady state [59]. By adopting supramolecular gelators into the LC media, the intrinsic advantages of anisotropic properties can be amplified by the integration of the reversibility and stability [60]. The supramolecules containing hydrogen bondable benzene-1,3,5-tricarboxamide core and light-responsive azobenzene mesogens were synthesized as a macrogelator [61]. The self-assembled columns formed by stacking the macrogelator along the hydrogen bonding directions. Continuous networks should be

Figure 5. Schematic illustration of surfactant molecules of AZ₁CE and AZ₂CE forming expanded and condensed phase on the ITO surfaces (a). 3D topographic height profiles of self-assembled AZ₁CE (b) and AZ₂CE (c) monolayer film. Reproduced with permission [57].
constructed to divide the nematic domain into many small clusters resulting in LC polydomains. Light scattering states have been obtained from a refractive index mismatch between the LC polydomains and randomly dispersed self-assembled fibres. Therefore, modulating the ordered structure of an LC physical gel in nanometre length scale can be applied as smart windows.

By optimising the content of the macrogelator, we fabricated a light shutter. The macrogelator is precipitated out of the LC molecules above the concentration of 2.5 wt%. On the other hand, the isotropic sol phase is observed below the 1 wt% of the macrogelator in the LC medium. This observation indicates that the fibrous networks cannot hold all the anisotropic molecules for the mechanically stable gel state. To demonstrate rewritable LC films, we optimise the content of the macrogelator in the LC medium as 1 wt% based on the phase behaviours. The optical cell is prepared by sandwiching 1 wt% macrogelator with ITO substrates without any alignment layers. At the initial stage, these films are very effective in scattering visible light, which results in a white state. When the UV light is irradiated through a patterned mask, the self-assembled columns of the macrogelator in the exposed area are dissociated by the conformational changes from trans to cis conformers (Figure 6a). Therefore, the nematic gel state is transformed into the nematic sol state at room temperature which results in light transmittance (Figure 6b). As a consequence, we can record a word on the LC film (Figure 6c). Even though Vis light is irradiated on the nematic sol state, the original nematic gel state is not fully recovered because the photorecorded phase is not a homogeneous state. In order to erase the photopatterned letters of ‘C’, the temperature is increased above the isotropic temperature. After cooling the isotropic liquid to room temperature, the light scattering state is observed again. We can find another letter of ‘U’ when the UV light is exposed through the corresponding photomask.

In the recent year, molecular engineering of photore sponsive polymers paves the new ways to develop the advanced materials [62]. Owing to the resolved photoisomerisation between trans and cis form, various photoresponsive polymers functionalised with the azobenzene have been reported as actuators that convert light to mechanical work [63]. It is widely accepted that phototriggered motion is decided by the initial orientation of chromophores [64]. Along this line, systematic studies on the hierarchical superstructures constructed by self-assembly of programmed building blocks offer new insights to determine the anisotropic bending direction [65]. To demonstrate photoactuators, we designed a polynorbornene containing the azobenzene side-chain dendron. This photoresponsive polymer (AZ₃NO) has a high molecular

![Figure 6. Fabrication procedure of photorecorders by applying a photomask (a). Transmittance changes of the LC cell filled with 1 wt% photoresponsive macrogelator by alternating UV and Vis light (b). Macroscopic images of the rewritable optical cell and possible mechanisms of LC gel formation and dissociation induced by light and heat (c). Reproduced with permission [61].](image-url)
weight ($M_n = 173$ kDa) and a low polydispersity index ($PDI = 1.05$). The ordered structure of AZ$_3$NO is confirmed by 2D WAXD patterns of the uniaxially oriented films (Figure 7a). The macroscopically oriented sample is prepared by a mechanical shearing process at 120°C. A series of small-angle diffraction peaks can be found on the meridian indicating the layer spacing of AZ$_3$NO is 5.96 nm. The reflection of $d = 0.43$ nm is found to be 60° away from the meridian in the quadrant, which illustrates that the azobenzene side chains are arranged in tilted fashion at room temperature. Strong birefringence of the POM images of the AZ$_3$NO should is due to the self-assembly of the polynorbornene main chains and the azobenzene side chains (Figure 7b).

Considering the hierarchical superstructure of the AZ$_3$NO, it is reasonable to understand the photomechanical work. Note that AZ$_3$NO in the highly ordered phases maintains the layer structure containing the smectic F like lateral molecular packing with 2D dimensions of $a = 0.77$ nm and $b = 0.55$ nm. The reflections peak at $d = 0.43$ assigned for (110) means that the azobenzene side chains are tilted 30° from the layer normal. As illustrated in Figure 7c, the azobenzene mesogens in the AZ$_3$NO film are almost aligned parallel to the film normal direction. Here, the UV light is irradiated perpendicular to the film direction. Since the cis isomer of azobenzene possesses the larger dimensions than the trans isomer in the identical plane, the photoisomerisation induces an increase in volume. At the same time, a grading of an absorption coefficient of the azobenzene makes uneven photoisomerisation through the film thickness. Therefore, the irradiation of UV light causes anisotropic surface expansion of the AZ$_3$NO film. As a result, it bends away from the light source when the AZ$_3$NO film is exposed to the UV light. Irradiation of Vis light restores the AZ$_3$NO film to its initial flat shape.

Figure 7. 2D WAXD patterns (a) and POM microphotographs (b) of AZ$_3$NO. Schematic illustrations of molecular packing model and photoreversible bending mechanisms upon irradiating UV and Vis light (c). Reproduced with permission [65].
In the information age, vast amounts of data are created on every day [66]. Digital optical disc is a prototypical example of recording for data storage, which use light to save the information [67]. Polymers including the conventional photoswitchable compounds are proposed to utilise in optical recording [68]. In general, the photoresponsive molecules can be switched between two isomeric states, representing ‘1’ and ‘0’ in the binary system [69]. A technical drawback of using the azobenzene compounds for storage media is due to the oxidation and other side reactions [70]. These photodamages can cause the information to delete during the multiple cycles of writing and erasing process of the photoswitchable material [71]. To overcome the problems of inefficient photoswitching processes, the photoresponsiveness of the chromophores should be improved in solid state [72]. The dissociation of the π-π stacked chromophores can usually lead to desirable photoresponse [73]. An alternative, using longer wavelength absorption dyes requiring low energy for photoisomerisation, has rarely been studied for optical storage [74]. Here, we adopt the first method, because the utilisation of best-known chemical is a facile way to prepare novel materials. Additionally, it provides us to another possibility to tune the photoresponsiveness depending on the packing structures of chromophores.

The photochromic LC polymer (AZ$_2$LP) consists of the azobenzene moiety, a phenol benzoate core, and flexible aliphatic chains as well as on the main chains (Figure 8a) [75]. Utilising computer simulation software (Cerius Accelrys), the molecular dimensions of a minimal energy geometry are estimated. The calculated length along the long axis is 2.39 nm. The mesogenic core of the azobenzene part is 1.54 nm. The long axis of the azobenzene pendant is located 40° away from the main chain. In the low angle region of the 2D WAXD fibre pattern at room temperature, two pairs of scattering halos at $d = 1.47$ nm have appeared on the four quadrants (Figure 8b). Their maximum intensities are located at 67°, 113°, 247° and 293° with respect to the meridian. This result indicates the fact that the nematic phase of AZ$_2$LP contains the local cybotactic fluctuations. Because of the long-range order only in 1D of AZ$_2$LP, the photochemical reaction has well occurred in the bulk state. To demonstrate the writing and erasing of certain patterns with light, uniform AZ$_2$LP films with 200 nm thickness are prepared by using a spin coating method on glass substrates. The patterned photomask is carefully placed between the UV source and the AZ$_2$LP film. Figure 8c shows a micropatterned AZ$_2$LP film. The UV-blocked region by the photomask reveals brownish in colour and exposed regions turn yellowish in colour. When the temperature is increased to 130°C and subsequently cooled to room temperature, the AZ$_2$LP film turns brownish in colour and the patterns are completely erased. Note that this process does not show the change in a patterning quality by more than a factor of 100, because of the reversibility of the photochemical reaction of the azobenzene chromophore.

4. Conclusions

Stimuli-responsive soft matters can be ideal candidates for applying in smart windows, flexible electronics, security printings, microactuators, and medical diagnostics.
Especially, photoresponsive molecules can change chemical and physical properties remotely by exposing light. This review introduced how to adjust the photoresponsive properties by controlling the phase behaviour and packing symmetry of azobenzene-based LC compounds from small molecules, to macromolecules and to supramolecules. The final photoresponsive properties of the programmed and precisely synthesised azobenzene-based LC derivatives are highly dependent on the self-assembled hierarchical superstructures. Although many researches and developments have been made on photoresponsive materials, more research, such as fast response, accurate operating direction and low energy consumption, is needed to put them into practical use.

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