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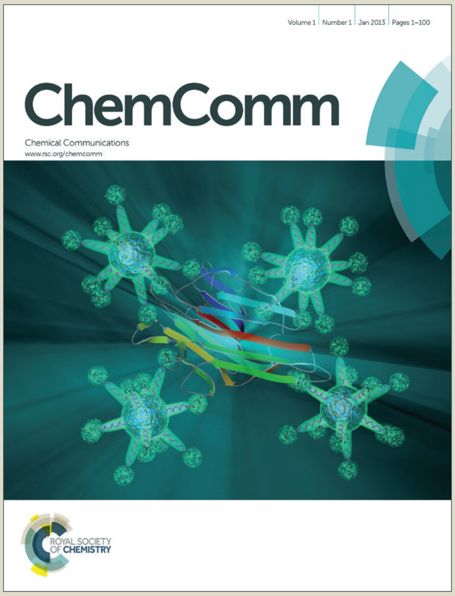

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Azobenzene-based photochromic liquid crystalline amphiphile for the remote-controllable light shutter

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By considering intramolecular conformations and intermolecular interactions, an azobenzene-based photochromic liquid crystalline amphiphile is synthesized for demonstrating the remote-controllable light shutter by the photo-induced isothermal phase transition between the highly ordered crystal phase and the isotropic liquid phase.

Since the physical, electrical, and optical properties of soft and hard materials strongly depend on their molecular organizations and conformations, the proper manipulation of material state has been one of the most fundamental and intriguing research fields for material scientists and engineers.[1] Phase transition of most organic compounds can be achieved by changing temperature under constant pressure. Particularly, partially ordered liquid crystalline (LC) soft materials can form the thermodynamically stable mesomorphic states between their crystalline (Cr) and isotropic (Iso) phases.[2] Recently, photochemically-induced phase transitions have become technologically attractive and important because of their remote-controllable optical properties.[3] Photochromic compounds such as azobenzene, spiropyran and diarylethene have been intensively studied as candidates for the direct photo-induced phase transformation. It is well known that the conformational change between *trans* and *cis* isomers of azobenzene can be applied to control the macroscopic molecular order.[4] However, the photo-reversible phase transition in the Cr phase is not easy because of the confined molecular packing structure and lack of molecular mobility. There are a few reports of direct photo-reversible transformation between solidus and liquidus phases.[5] Therefore, the light-induced phase transition of soft materials have been focused on the LC-to-LC phases, the LC-to-Iso phases, and the gel-to-sol phases.[6]

In this context, we challenge to develop a novel photochromic material which can be reversibly changed between solidus and liquidus states by light. It is worth mentioning the fact that phase transition behaviours are strongly influenced by molecular shape and packing symmetry.[7] By taking into account of intramolecular conformations and intermolecular interactions, we propose a photo-responsive amphiphilic molecule (abbreviated as CAz-OH) for the remote-controllable light shutter (Fig. 1). The synthetic and purification methods were summarized in Fig. S1-S6 of the ESI and more detail information is provided in our recent report.[8] As shown in Fig. 1b, CAz-OH molecule basically consists of three different segments: the photochromic rigid azobenzene mesogen, the flexible hydrophobic alkyl tail, and the flexible hydrophilic ethylene oxide chain. Especially, by introducing hydroxyl function at the end of ethylene oxide chain, the amphiphilic nature of CAz-OH compound can dramatically enhance the nanophase separation within the molecule and form the dimeric building block due to the intermolecular hydrogen (*H*)-bonds. Furthermore, the flexible ethylene oxide side chains and alkyl tails chemically attached to the azobenzene mesogen tend to increase the molecular mobility even at ambient conditon.[9] Assuming the all-*trans* conformation, the length of CAz-OH is 3.31 nm along the longitudinal axis (Fig. 1c).

Because the photo-induced phase transitions of CAz-OH are closely related to the reorganization of neighbouring molecules *via* the photo-isomerization, it is worthy to know the molecular packing structures of CAz-OH at different phases.[10] Thermal transition behaviours of CAz-OH are investigated by differential scanning calorimetry (DSC, Fig. S7) and polarized optical microscopy (POM, Fig. 2). The thermal transition at 98 °C is independent of the cooling rate, which is often observed from the Iso phase to a LC phase transition. On the other hand, the onset transition temperature and its corresponding heat at low temperatures exhibit the supercooling effect during the crystallization process.[11] Thermodynamic properties obtained from the subsequent heating process are consistent with those from the cooling process. As shown in Fig. 2a, POM at 95 °C shows a domain texture exhibiting a typical smectic (Sm) LC phase.[12] Strong birefringent aggregates are obtained upon decreasing the temperature to 25 °C. The transition temperatures and corresponding phase structures are summarized in Fig. 1a.

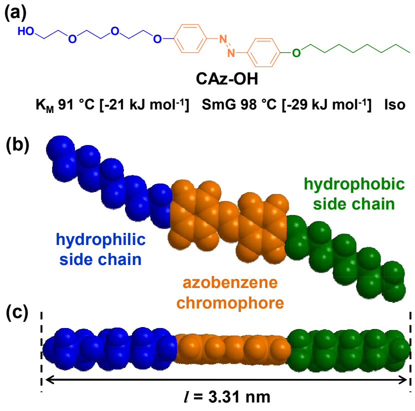

Fig.1 Chemical structures, phase transition temperatures and the corresponding enthalpies of CAz-OH molecule (a). Computer energy-minimized geometric dimensions of CAz-OH in the views from front (b) and side (c) directions, respectively. Abbreviations: K_M = monoclinic crystal phase, SmG = highly ordered smectic G liquid crystal phase, and Iso = isotropic liquid phase.

The temperature-dependent structural evolutions of CAz-OH are monitored with one-dimensional (1D) wide-angle X-ray diffraction (WAXD). As represented in Fig. 2b, CAz-OH exhibits two amorphous halos at 2θ = 2.65° (d = 3.33 nm) and 19.8° (d = 0.44 nm) above 120 °C, which correspond to the average longitudinal periodicity of electron density fluctuations among the nanophase separated CAz-OH and to the average lateral distance between amorphous azobenzene mesogens, respectively.[13] The Iso state is further confirmed by the complete dark state under POM. Just below the isotropization temperature, two apparent low-angle reflections at 2θ = 2.06° (d = 4.29 nm) and 2.65° (d = 2.14 nm) in addition to four high-angle reflections at 2θ = 18.1° (d = 0.49 nm), 19.2° (d = 0.46 nm), 20.4° (d = 0.43 nm) and 21.8° (d = 0.40 nm) indicate that a highly ordered Sm LC phase is formed. Many sharp reflections detected at 25 °C in the wide-angle region represent that a true Cr structure is formed (Fig. 2b).

To understand molecular packing structures in the ordered phases, 2D WAXD fibre pattern is obtained by irradiating X-ray perpendicular to the shear direction (SD) of the macroscopically oriented CAz-OH sample. As shown in Fig. 3a, a pair of diffraction peaks at 2θ = 2.22° (d = 3.97 nm) is observed on the meridian together with its higher order diffractions (2θ = 4.44°, 15.5° and 17.7°). This result indicates that the diffraction at 2θ = 2.22° is attributed to the layered structure of which layer normal is parallel to the SD. Note that one CAz-OH molecule is 3.31 nm in length which is estimated by a computer energy minimization utilizing the COMPASS force field of Cerius^2 software (Fig. 1c). Therefore, the building block of layer structure should be a dimer. This analysis can be further supported by the head-to-head dimer formation *via* the intermolecular *H*-bonding between the hydroxyl groups (-OH) of two molecules.[14]

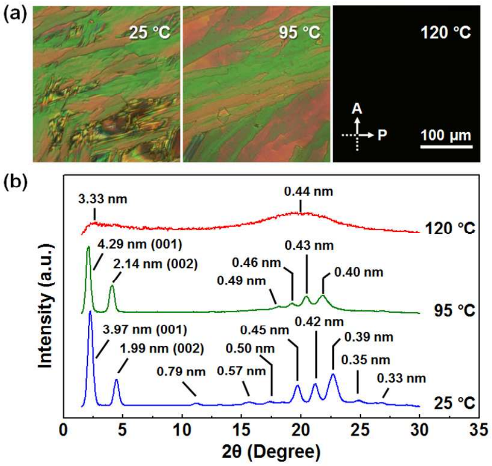

Fig. 2 POM images of CAz-OH during the cooling process (a) and its 1D WAXD patterns (b) at different temperatures.

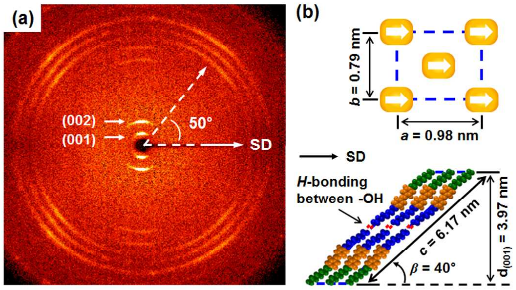

Fig. 3 2D WAXD pattern of the crystalline phase of CAz-OH at room temperature (a) and a schematic illustration of molecular arrangement in the crystal (b).

Since the layer spacing is 3.97 nm, the dimeric building blocks in the layer must be interdigitated and tilted away from the layer normal.[15] As shown in Fig. 3a, the reflection in the quadrant is found to be 40° away from the meridian, which means that the bilayered CAz-OH building blocks are tilted 50° away from the layer normal direction. The detail structure analysis based on the 2D WAXD pattern of oriented CAz-OH sample indicates that this crystal possesses a monoclinic lattice with the dimensions of a = 0.98 nm, b = 0.79 nm, c = 6.17 nm, α = 90°, β = 40° and γ = 90° (Fig. 3b). It is realized that the dimers are synclinically tilted layer-by-layer and form a smectic H (SmH)-like Cr phase (assigned as the K_M phase). Since the free volume creations and conformation changes would take an enormous amount of energy, the molecular packing structure of the highly ordered LC phase at 95 °C should be similar to that of K_M phase at 25 °C. From the combined results of WAXD, DSC, and POM, it is found that CAz-OH dimers are also synclinically tilted layer-by-layer but the layer is slightly expanded from d = 3.97 nm to d = 4.29 nm. Additionally, it is obvious that the molecules are tilted towards a face, not an apex (Fig. 3b). On the basis of experimental results, it is concluded that the molecules in the highly ordered LC state at 95 °C construct the dimeric building block and laterally pack in the fashion of smectic G (SmG)-like structure with the monoclinic unit cell dimensions of a = 0.91 nm, b = 0.76 nm, c = 6.05 nm, α = 90°, β = 45° and γ = 90° (Fig. S8).[16]

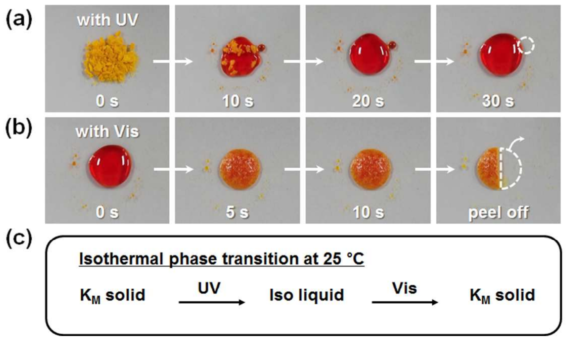

Fig. 4 Photo-induced solidus to liquidus phase transition of CAz-OH crystal under the UV light irradiation for 20 s (a) and subsequent liquidus to solidus phase transition of CAz-OH liquid by irradiating Vis light for 10 s (b). Photo-induced phase transition behaviours of CAz-OH at room temperature (c).

Since the azobenzene and its derivatives undergo a reversible phase transformation by the *trans-cis* photo-isomerization, we expect that the K_M solid and Iso liquid states can be reversibly converted by transforming molecular conformations of CAz-OH, which can be applied for the fabrication of remote-controllable optical devices. The photochemical behaviours of CAz-OH are fully analyzed by UV-Vis spectroscopy and the results are summarized in Fig. S9 and Fig. S10. However, for the practical applications of CAz-OH in optical devices, the efficient *trans-cis* photo-isomerization should occur even in its solid state. Therefore, the photo-induced phase transition in the solidus K_M phase are investigated at ambient condition.

As shown in Fig. 4a, the K_M phase of CAz-OH powder rapidly turns to a liquidus droplet by irradiating the UV light (200 mW cm^{-2}). The 20 s irradiation time is enough to induce the CAz-OH liquidus state. In order to reduce the surface energy, the fluidic CAz-OH droplets are merged together to form a single droplet (Fig. 4a), which is one of the prominent characteristics of liquid state. The absorption spectra of CAz-OH in solidus state with respect to the UV light irradiation ensure the photo-induced phase transition and their corresponding color changes (Fig. S11). As exposing the UV light, the absorption maximum (π-π*) of the resultant yellow solid at 335 nm is decreased by concomitantly increasing the intensity of absorption band for *cis* isomer (n-π*) in the orange liquid (455 nm). Note that the light is absorbed in the specific wavelength ranges by CAz-OH and the rest of light passes through to reach the eyes. From the POM observations, it is obvious that the liquidus state does not show optical anisotropy, but the Iso melt state (Fig. S12). When the irradiated UV light is blocked, the liquidus droplet of CAz-OH immediately returns back to the solidus state within 10 s (Fig. 4b). Here, the crystallization process can be accelerated by irradiating Vis light. Absorption bands are completely recovered to the initial state with the irradiation of light at 450 nm (Fig. S11). The CAz-OH solid is easily peeled off without losing its shape, which is one of the representative characteristics of solidus state. The photo-induced reversible phase transition behaviours of CAz-OH between K_M and Iso states are summarized in Fig. 4c.

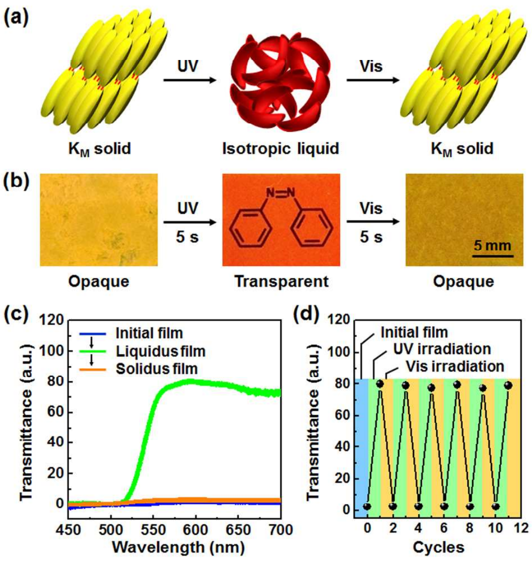

Fig. 5 Schematic illustration of photo-induced phase transition behaviours of CAz-OH at room temperature (a). Photographs of the photo-reversible light shutter upon tuning the wavelength of light at room temperature (b). Transmittance change (c) and its corresponding light modulating efficiency (d) of CAz-OH film demonstrating the photo-reversible phase transition under the UV and Vis light irradiation in 5 s at room temperature.

The photo-switching processes between K_M solid and Iso liquid states of CAz-OH can be explained by a molecular packing structure. By irradiating UV light to the K_M phase, the stable bilayered structure (d = 3.97 nm) is suddenly collapsed by the dissociation of intermolecular *H*-bonds (d = 3.33 nm), which is triggered by the transformation from *trans* to *cis* conformers of CAz-OH (Fig. S13).[17] Since the longitudinal chains chemically connected to the azobenzene chromophore are flexible ethylene oxide and alkyl chains, the transformation from *trans* to *cis* conformers is easily initiated and accelerated for the photochemical transformation of neighbouring molecules by providing the enough mobility. Furthermore, the *cis* isomerized metastable CAz-OH molecules in advance play a key role as the solvent-like molecules. It generates huge amplifications for breaking the molecular packing symmetry of the remaining stable *trans* CAz-OH conformers. Finally, the long-range molecular orders are totally disappeared, resulting in the photochemical phase transition from K_M to Iso phases on the order of second. When the irradiated UV light is blocked, the Iso phase quickly returns back to the initial K_M phase, which process is mainly driven by the recrystallization force and the intermolecular *H*-bonding formation. Based on the absorption spectra (Fig. S11) combined with POM photographs (Fig. S12) and WAXD patterns (Fig. S13), it is realized that the highly ordered K_M phase of CAz-OH molecules before and after the photo-induced phase transition is almost identical. The photochemical switching processes of CAz-OH are schematically illustrated in Fig. 5a.

To test the light modulating property of CAz-OH, the optical test cells with 50 μm thickness and 10 × 10 mm^2 dimensions are fabricated by directly loading the CAz-OH compound. Fig. 5b shows the photographs of the CAz-OH film working as a light shutter by alternating UV and Vis lights. By tuning the wavelength of light, both opaque Cr and transparent Iso states reversibly transit to one another in less than 5 s. The image of the graphical formula "azobenzene" behind the light shutter is clearly discernible in the transparent Iso state and the light shutter completely blocks the behind image by the light scattering of the K_M solid state. The liquidus state of CAz-OH film induced by UV light transmits the incident light. As shown in Fig. 5c, the transmittance intensity of photo-induced liquefied film is about 40 times higher than that of the initial solidus film. The photo-reversible switching of transmittance light across visible wavelength region is repeated many times without any noticeable degradations (Fig. 5d).

In summary, a specifically programmed amphiphilic CAz-OH LC molecule is newly designed and synthesized for demonstrating the direct photo-reversible phase transition between crystalline solid and isotropic liquid. From the systematic analyses with DSC, POM and WAXD, the phase transition behaviours of CAz-OH molecule at different temperatures are identified: one is the crystalline K_M phase with a monoclinic lattice at low temperatures and the other is the highly ordered SmG LC phase at high temperatures. In addition, the photo-reversible isothermal phase transition behaviours of CAz-OH have been successfully demonstrated for the remote-controllable light shutter. Finally, it is concluded that understanding the relationship between chemical structure and molecular packing symmetry is critical to design the suitable photo-responsive materials for the practical applications in optical devices.

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