



# Photoswitchable solvent-free DNA thermotropic liquid crystals toward self-erasable shape information recording biomaterials



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## ABSTRACT

Soft thermotropic liquid crystals (TLCs) have advantages on processability and shape memory compared to hard solids and fluids. The development of photoswitchable soft TLCs based on biomolecules would afford reworkable shape information recording biomaterials for the areas requiring biocompatibility and degradability. In recent years, anhydrous DNA TLCs composed of DNA and ammonium surfactants have been receiving continuous attention. However, the photoswitchable phase transition has not been realized for soft DNA TLCs at room temperature, owing to the absence of functional ammonium surfactant. Herein, a new type of azobenzene-containing surfactant would be applied to the fabrication of soft DNA TLCs with photoresponsive physical properties. The double-chain design of the used surfactant and the use of DOAB as a dopant guarantee the soft state of DNA TLCs at r.t., which also facilitates the azobenzene isomerization by reducing the packing density of surfactants. With the assistance of photoisomerization of azobenzene, the reported DNA TLCs achieve reversible liquid crystal-isotropic liquid transition at temperatures below clearing points even at room temperature. The repeatable shape information recording and self-erasing tests indicate these DNA TLCs would be good shape information recording biomaterials in the future. This work also provides a useful strategy for designing photo-responsive soft biomaterials based on rigid biomolecules like DNA.

## 1. Introduction

Soft thermotropic liquid crystal (TLC) materials have advantages over solid materials and fluids in some ways. Solid materials are ideal hard coatings and structural elements but showing a shortage of processability [1]. Fluids show superior processable and healable properties than materials in other physical states, but without the ability to maintain the important information for materials, like the designated shapes, due to the absence of ordered structure. Compared to solid materials and fluids, soft TLCs gain a good balance on the processability and information storage ability. For example, a shape print on the surface of TLCs could be easily achieved and be well kept over a period. For soft TLCs, the photoswitchable liquid crystal  $\rightleftharpoons$  isotropic liquid (LC  $\rightleftharpoons$  IL) phase change property is of great importance, which could enable TLCs reworkable in practical application.

As one type of emerging ionic liquid crystals [2], solvent-free DNA TLCs have been receiving continuous attention in recent years [3–10],

which might afford alternatives for the materials desiring biocompatibility, degradability, and especially, water-free condition, for example, being substitutes to some polymeric ionic liquids [11], wound dressings [12] and self-healing biomaterials [13]. The solvent-free DNA TLCs are composed of anionic DNA and cationic surfactants via electrostatic complexation. Although these materials could give reversible LC  $\rightleftharpoons$  IL phase change via the fine control on temperature, the relatively high clearing points largely limit their potential applications, based on the consideration that a high temperature would be detrimental to the physiological activities of creatures. Therefore, the development of solvent-free DNA TLCs with isothermal phase change ability at or near room temperature (r.t.) becomes imperative.

In the past decade, by achieving various purposes, isothermal phase change has been realized in several kinds of materials through the *trans*  $\rightleftharpoons$  *cis* photoisomerization of azobenzene (AZO), including polymers [1,14,15], nanomaterials [16], single compounds [17,18], and surfactants [19]. It is worth noting that these reported AZO-containing

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materials present as solid at r.t., probably due to the accumulation of  $\pi$ - $\pi$  interactions among AZOs, as well as the existed van der Waals force. Thus, to obtain photoswitchable solvent-free DNA materials in a soft liquid crystalline state at r.t., a delicate molecule design on the AZO-containing surfactant is of necessity because the external stimuli-responsive ability of TLCs relies on the mobility part that refers to surfactant in DNA TLCs [20]. The development of soft DNA TLCs with the photoswitchable property was launched in 2017 by us [7]. Unfortunately, the initially reported AZO-containing DNA TLC showed neither phase change nor surface topography change, owing to the insufficient molecular flexibility of the applied AZO surfactant. Additionally, the low synthetic yield that results from the low water solubility of surfactant largely limits its further application. In somehow, this could be deemed as the first idea proposed on this topic.

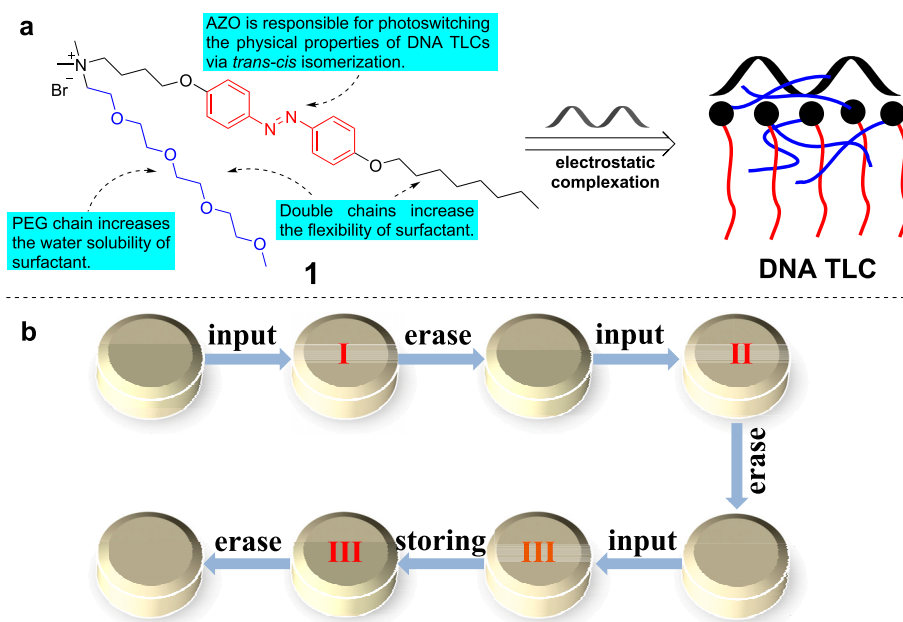
In this present study, a new type of AZO-containing DNA TLCs would be synthesized via the use of surfactant **1** (Fig. 1a). The double chains of **1** provide sufficient molecular flexibility, leading to soft DNA TLCs at r.t. by reducing the packing density of surfactants. The design of one polyethylene glycol (PEG) chain other than the alkyl chain increases the water solubility of **1**, facilitating the complexation with DNA in aqueous conditions. With the assistance of *trans*  $\rightleftharpoons$  *cis* AZO isomerization, the reported DNA TLCs achieved reversible isothermal phase transitions and mechanical property changes at temperatures

below their clearing points, even at r.t. The reported soft DNA materials could be good shape information recording biomaterials with self-erasable property, affording candidate information materials for the areas requiring biocompatibility or degradability, for example, being as smart tags for packaging perishable foods or medical products [21] (Fig. 1b). With this work, we would like to provide a designing strategy for obtaining soft functional biomaterials with photo-switchable physical properties at r.t.

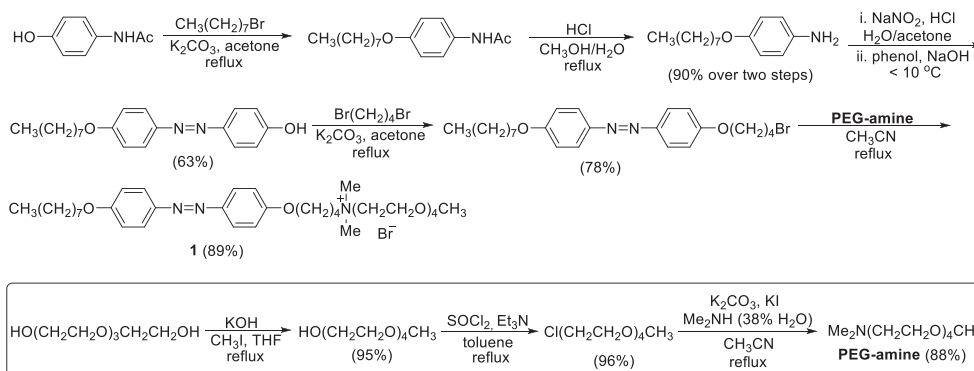
## 2. Material and methods

### 2.1. Synthesis of ammonium surfactant **1**

Surfactant **1** was prepared in 39% yield over 5 steps according to our reported synthetic route [22] (Scheme 1). The NMR of synthesized surfactant **1** showed good consistency with that of previously reported one.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.84–7.82 (m, 4 H), 6.98–6.95 (m, 4 H), 4.09 (t,  $J = 6.0$  Hz, 2 H), 4.01–3.95 (m, 4 H), 3.88–3.87 (m, 2 H), 3.76–3.72 (m, 2 H), 3.64–3.62 (m, 2 H), 3.57–3.56 (m, 8 H), 3.50–3.49 (m, 2 H), 3.38 (s, 6 H), 3.33 (s, 3 H), 2.03–1.97 (m, 2 H), 1.92–1.89 (m, 2 H), 1.81–1.76 (m, 2 H), 1.48–1.42 (m, 2 H), 1.35–1.23 (m, 8 H), 0.87 (t,  $J = 6.5$  Hz, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.2, 160.4, 147.1, 146.7, 124.3, 114.62, 114.60, 71.8, 70.4, 70.33, 70.30, 70.28, 70.1, 68.3,



**Fig. 1.** (a) The chemical structure of AZO-containing surfactant **1**, and schematic illustration on the fabrication of DNA TLC via electrostatic complexation between DNA and **1**. (b) Schematic illustration on the soft DNA TLC showing shape information recording and self-erasable properties.



**Scheme 1.** The synthesis of ammonium surfactant **1**.

67.0, 65.4, 64.9, 63.2, 58.9, 51.9, 31.7, 29.3, 29.14, 29.12, 25.93, 25.86, 22.6, 19.8, 14.0.

## 2.2. Synthesis of DNA TLCs

The aqueous solution of **1** (28.7 mM, 115  $\mu$ L) was added into the aqueous DNA (5'-CCTCGCTCTGCTAATCCTGTTA-3') solution (1.5 mM, 20  $\mu$ L) using a pipette, which led to the precipitate of DNA-**1** complex. The precipitate was collected by centrifugation with rcf of 6124 g in an H1-16 KR Centrifuge from Hunan Kechengyiqi Co., Ltd, China. The obtained precipitate was washed with water and centrifuged over three times. The resultant wet precipitate was pretreated with liquid nitrogen and then put into a SCIENTZ-10 N Lyophilizer from Ningbo Scientz Biotechnology Co., Ltd, China, for a lyophilization with  $-80$   $^{\circ}$ C overnight, affording the needed DNA-**1** (1:5) TLC.

DNA-**1**-DOAB (1:x:y) was prepared following a procedure as that of DNA-**1** (1:5) TLC, but using **1** (28.7 mM, 92  $\mu$ L) and DOAB (60 mM, 11  $\mu$ L) for DNA-**1**-DOAB (1:4:1), **1** (28.7 mM, 69  $\mu$ L) and DOAB (60 mM, 22  $\mu$ L) for DNA-**1**-DOAB (1:3:2), **1** (28.7 mM, 46  $\mu$ L) and DOAB (60 mM, 33  $\mu$ L) for DNA-**1**-DOAB (1:2:3), **1** (28.7 mM, 23  $\mu$ L) and DOAB (60 mM, 44  $\mu$ L) for DNA-**1**-DOAB (1:1:4), respectively.

## 3. Results and discussion

### 3.1. Synthesis and characterizations of **1**

Ammonium surfactant **1** was prepared as an orange solid in 39% overall yield over five steps starting from the commercially available 4-acetoamidophenol, following our designed synthetic strategy [22] (Scheme 1). In brief, the phenol was subjected to etherification, hydrolysis, diazotization, bromoalkylation, and a final treatment with *N,N*-dimethyl-2,5,8,11-tetraoxatridecan-13-amine to accomplish **1**. Thanks to the introduction of the hydrophilic PEG chain, **1** is a good surfactant candidate for the fabrication of solvent-free DNA TLCs by showing good water solubility.

The photoisomerization of **1** was investigated in an aqueous solution employing UV-vis absorption spectroscopy measurement. Initially, **1** gave a strong absorption band centered at 360 nm corresponding to the  $\pi$ - $\pi^*$  absorption (Fig. 2a). Under UV light illumination (365 nm), **1** showed very fast *trans*  $\rightarrow$  *cis* isomerization, which could reach the photostationary state in 15 s by giving decreased  $\pi$ - $\pi^*$  absorption band and new formation of  $n$ - $\pi^*$  absorption band at 445 nm. Vis light illumination (520 nm) on **1** could furnish the *cis*  $\rightarrow$  *trans* isomerization efficiently by showing increased  $\pi$ - $\pi^*$  absorption band along with diminishing the  $n$ - $\pi^*$  absorption (Fig. 2b). In 50 s, **1** reached its original state completely. It is worth noting that we did not determine the isomer ratios for the photostationary states under UV and vis light irradiations, based on the following considerations: (1) surfactant **1** is prepared for the fabrication of solvent-free DNA TLCs, in which **1** would be in a completely different system compared to the aqueous condition, while, the solvents or condensed ionic surroundings impact the isomer ratio of AZO dramatically; (2) a very low concentration of **1** was applied in an aqueous condition in order to avoid the self-assembly that causes the absorption intensity change and peak shifting, while, in the solvent-free DNA TLCs **1** would be in the condensed state; (3) in these two systems the UV light penetration efficiency would be in great difference.

The thermal properties of **1** were investigated by Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). In the DSC profiles of **1**, the two endothermic peaks at 84  $^{\circ}$ C and 138  $^{\circ}$ C indicate the melting point for Crystal  $\rightarrow$  LC transition and clearing point for LC  $\rightarrow$  IL (Fig. 2c). The clearing point of **1** was further confirmed by temperature-dependent polarized optical microscopy (POM) analysis (Fig. S1). TGA analysis of **1** revealed its water content of <2% (wt) and indicated the thermal integrity up to 190  $^{\circ}$ C (Fig. 2d).

### 3.2. Synthesis and characterizations of DNA TLCs

Solvent-free DNA TLCs were fabricated by using 22-mer single-stranded DNA and ammonium surfactants (**1** and dioctyldimethylammonium bromide (DOAB)) via (1) electrostatic

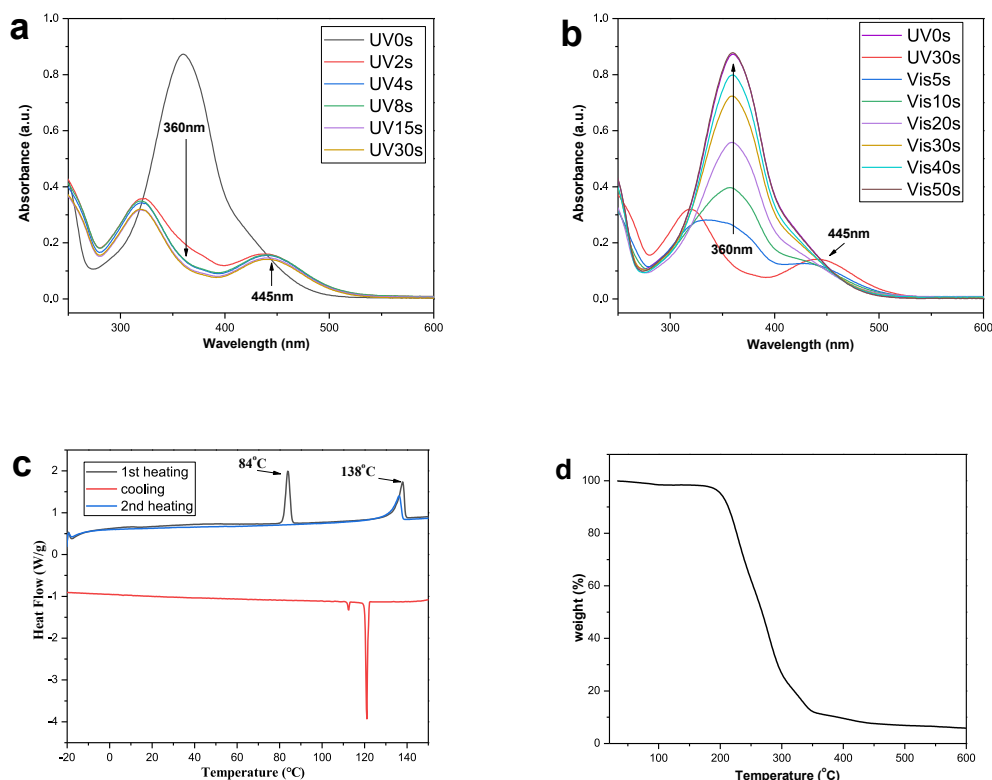
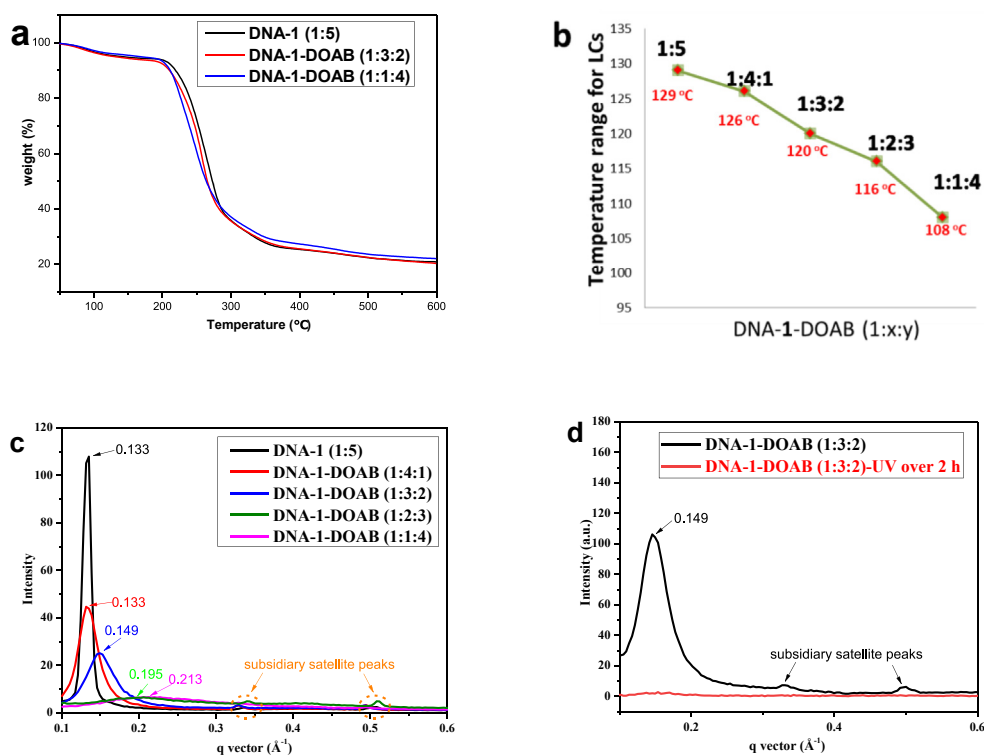


Fig. 2. Characterizations of surfactant **1** (aq, 43.9  $\mu$ M) (a) under UV and (b) under vis light irradiations, respectively. (c) DSC traces of **1** recorded by two thermal cycles with a heating-cooling rate of 5  $^{\circ}$ C min $^{-1}$ . (d) TGA profile of **1**.



**Fig. 3.** Characterizations of DNA-1-DOAB TLCs. (a) TGA profiles of DNA-1-DOAB TLCs. (b) Temperature ranges for thermodynamic stable liquid crystalline states of DNA-1-DOAB TLCs. (c) SAXS profiles of DNA-1-DOAB TLCs. (d) SAXS profiles of DNA-1-DOAB (1:3:2) before and after UV illumination over 2 h at r.t.

complexation in aqueous solution, (2) centrifugation, and (3) lyophilization of the resulted precipitates. In the solvent-free DNA-surfactant TLCs, DNA is the rigid part responsive for introducing orientational anisotropy, and the flexible surfactants make up the flexibility responsive for the suppression of crystallization [3,20]. Therefore, the use of short sequence DNA is necessary for obtaining photoresponsive liquid crystalline ionic DNA melts at r.t. On the one hand, short sequence DNA would introduce less viscosity into DNA materials, leading to the formation of soft melts that have less power on maintaining the order structure than hard crystals. On the other hand, if a long sequence DNA was applied, the DNA skeleton would complex with more surfactants, which results in a great accumulation of van der Waals force among aliphatic chains and  $\pi$ - $\pi$  force among AZOs, largely inhibiting the photoisomerization of AZOs by the formation of highly condensed arrangement of surfactants.

All the prepared DNA TLCs are presented as DNA-1-DOAB (1:x:y), according to the used stoichiometric charge ratio of DNA:1:DOAB during the sample fabrication. For instance, DNA-1-DOAB (1:3:2) represents the DNA TLC fabricated by the complexation of DNA 1, and DOAB in the charge ratio of 1:3:2. In this study, five types of DNA TLCs showing a liquid crystalline state at r.t. were designed and prepared, which are DNA-1 (1:5), DNA-2-DOAB (1:4:1), DNA-1-DOAB (1:3:2), DNA-1-DOAB (1:2:3), and DNA-1-DOAB (1:1:4), aiming at searching for the photoresponsive phase change DNA TLC at r.t. Without using DOAB, the  $\pi$ - $\pi$  force would promote the formation of a high packing density of 1, which causes difficult photoisomerization of 1 by leaving insufficient free volume for the AZO motif. Doping DOAB with double aliphatic chains into the DNA materials could break the  $\pi$ - $\pi$  force among 1, facilitating the photoisomerization of AZOs through softening the material. Meanwhile, it is also worth noting that the photoregulated phase change ability of DNA TLCs might also be lost if introducing too much DOAB, as the ‘working groups’ become insufficient. Based on these considerations, we screened DNA-1-DOAB (1:x:y) by gradually increasing the charge ratio of DOAB, searching for the best candidate DNA TLC with photoswitchable LC  $\rightleftharpoons$  IL phase transition property at r.t.

The thermal properties of DNA-1-DOAB TLCs were firstly investigated by TGA analysis (Fig. 3a). Their water contents are less than 5%, and thermal integrities are higher than 200 °C. The melting points and clearing points of DNA-1-DOAB TLCs were determined by DSC measurements and temperature-dependent POM analysis (Fig. S2). The results clearly show that all the prepared DNA TLCs are LCs at r.t. by giving melting points below 0 °C. For the prepared DNA materials, an interesting correlation between the width of the temperature window for the thermodynamic liquid crystalline stability and the ratio of 1 in the DNA materials was found in this study (Fig. 3b). Along with the decrease of 1, the temperature window for the LC phases of DNA-1 (1:5), DNA-1-DOAB (1:4:1), DNA-1-DOAB (1:3:2), DNA-1-DOAB (1:2:3) and DNA-1-DOAB (1:1:4) decreases from 129 °C to 108 °C. This phenomenon could be explained by the decreased  $\pi$ - $\pi$  force among AZOs along with the less use of 1, as  $\pi$ - $\pi$  force is a stronger power than van der Waals force for maintaining the order arrangement of surfactants. It is worth pointing out that the temperature ranges of liquid crystalline states of these DNA TLCs are much wider than that of AZO-containing surfactant 1, at least doubled (129–108 °C VS 54 °C).

The ordered structures of DNA-1-DOAB TLCs were characterized by SAXS (Fig. 3c). Broad diffraction peaks ranging from 0.133 to 0.213  $\text{\AA}^{-1}$  with no following harmonics were observed for DNA-1 (1:5) to DNA-1-DOAB (1:1:4), indicating the nematic arrangement, which is in accordance with the reported AZO-containing solvent-free biomaterials from our previous studies [7,23]. The diffraction peaks correspond to the diffraction spacing distances from 4.72 to 2.95 nm, which decrease along with the ratio decrease of 1 in the DNA materials. These spacing distances are composed of 1.1 nm thickness of DNA [24] and 3.62 to 1.85 nm thickness of surfactants, of which the thickness of surfactants is dominated by 1 with a gradual transition to DOAB for samples from DNA-1 (1:5) to DNA-1-DOAB (1:1:4) [4]. Additionally, two groups of peaks at  $\sim 0.34 \text{\AA}^{-1}$  and  $\sim 0.51 \text{\AA}^{-1}$  regions were also observed, while the ratio between these peaks and broad diffraction peaks does not correspond to a layered structure. We attribute them to the harmonic peaks of the first-ordered subsidiary satellite peaks of nematic diffraction peaks,

indicating an in-plane layer undulation for the DNA materials, of which the first-order subsidiary satellite peaks are probably overlapped by the broad diffraction peaks.

### 3.3. Reversible photoresponsive phase transitions of DNA TLCs

Due to the strong  $\pi$ - $\pi$  force among AZOs, the solvent-free AZO-containing phase change materials are normally present in a solid-state at r.t. [1,14–18,25,26]. In this study, the applied DNA is more structurally rigid than the previously reported polymeric networks or single compounds, such as polyacrylates [1] and sugar alcohols [17]. A rigid structure provides more power on maintaining the ordered structure, leading to difficult isothermal phase change under photoillumination. Therefore, without using AZO-containing surfactant with good flexibility, the DNA-surfactant complex could hardly gain the phase change ability below the clearing point. By employing a double-flexible-chain designing strategy, we herein report a new class of AZO-containing solvent-free soft DNA TLCs at r.t., which could exhibit various photoregulated phase change properties depending on the composition of the materials.

The isothermal LC  $\rightleftharpoons$  IL phase transitions of DNA-1-DOAB under light conditions were mainly analyzed by POM (Fig. S3). DNA-1 (1:5) showed very difficult photoresponsive phase changes at temperatures below 60 °C (Fig. S3–A). Without fabricating DOAB, the high packing density of surfactants leaves insufficient free room for AZO isomerization, which also largely limits the UV penetration into DNA material [27], owing to the powerful  $\pi$ - $\pi$  force among 1. To facilitate the AZO isomerization in DNA TLCs, we introduced DOAB to break the highly packed AZO surfactant 1 [28]. As is expected, DNA-1-DOAB (1:4:1) gave more efficient athermal phase change by forming IL under UV light over 30 min at 40 °C (Fig. S3–B). It is worth noting that both DNA-1 (1:5) at 60 °C and DNA-1-DOAB (1:4:1) at 40 °C could restore their ordered structure from IL state, as a result of thermal condition induced *cis-trans* AZO isomerization. A photoresponsive phase crossover at r.t. was accomplished with DNA-1-DOAB (1:3:2), by forming an IL state over 20 min UV light illumination and reverting LC state back over 18 min thermal isomerization or 1 min vis light illumination (Fig. 4a). SAXS measurements confirmed the disappearance of the ordered structure of DNA-1-DOAB (1:3:2) after UV irradiation (Fig. 3d). Fabricating more DOAB than 1, DNA-1-DOAB (1:2:3) and DNA-1-DOAB (1:1:4) lost the effective photoresponsive phase change ability at r.t (Fig. S4), but exhibited faster phase change from LC to IL at 40 °C (Fig. S3D and E), thanks to the much decreased  $\pi$ - $\pi$  forces along with less use of 1. However, as an unwilling result, the formed ILs of DNA-1-DOAB (1:2:3) and DNA-1-DOAB (1:1:4) hardly gain the ordered LC state back at 40 °C, probably resulted from the absence of sufficient functional AZO surfactants. An observation of the recovery of an ordered structure after cooling the DNA-1-DOAB (1:2:3) and DNA-1-DOAB (1:1:4) ILs to r.t. from 40 °C indicates that their TLC

properties were not affected (Fig. S5).

### 3.4. Rheological analysis on DNA material

Photoregulative mechanical property change at r.t. is of great importance for the practical application of biomaterials in various areas, considering the body temperature and living environmental temperatures of creatures. For the previously reported solvent-free AZO-containing DNA materials, no mechanical property change has been detected by the dynamic mechanical analysis employing a shear rheometer, as these samples could not give isothermal phase change at r.t. [7].

The mechanical property changes of DNA-1-DOAB (1:3:2) were subjected to viscoelasticity studies employing a shear rheometer. The elastic portion and viscous portion were determined by the storage ( $G'$ ) and loss ( $G''$ ) moduli, respectively. At r.t., DNA-1-DOAB (1:3:2) behaved liquid-like property, indicated by the larger  $G''$  than  $G'$  over the measured frequency range (Fig. 4b, red curves). A UV photoirradiation over 30 min led to significantly decreased  $G''$  and  $G'$ , but still maintaining its liquid-like property (Fig. 4b, blue curves). Under vis light irradiation, the ordered structure of DNA-1-DOAB (1:3:2) would be recovered with high efficiency. However, a full recovery of mechanical property becomes difficult, by showing a partial restoration of both  $G''$  and  $G'$  values over 10 min vis light irradiation (Fig. S6). This slow mechanical property change under vis light might be caused by a slow 'crystallization' process [29]. Rheological analysis on DNA-1-DOAB (1:3:2) reveals the newly developed DNA melts are good phase change biomaterials with photoresponsive mechanical properties.

### 3.5. Mechanism explanation on the isothermal phase changes of DNA TLCs

In contrast to the clearing points of DNA TLCs above 100 °C for DNA-1 (1:5) to DNA-1-DOAB (1:1:4), we achieved the photoinduced formation of ILs far below their clearing points, even at r.t. In order to confirm this process resulted from the photoisomerization of 1 other than the heating from UV light, the photothermal effect of applied UV light was investigated by an infrared thermometer, following a reported procedure [1] (Fig. S7). The surface temperature of testing samples would slowly increase to 26 °C from 24 °C after 90 min UV irradiation (31.8 mW cm<sup>-2</sup>), which means that the photothermal effect of applied UV light in this study is kind of negligible. Therefore, the isothermal LC  $\rightarrow$  IL phase transition of DNA-1-DOAB is the sole result of UV light-induced *trans*  $\rightarrow$  *cis* AZO isomerization of 1.

As shown in Fig. 5, surfactants of 1 and DOAB complex with DNA via electrostatic interaction, of which the van der Waals force and  $\pi$ - $\pi$  interaction among surfactant molecules maintained the ordered arrangement. At r.t., DNA-1-DOAB (1:3:2) affords sufficient free room

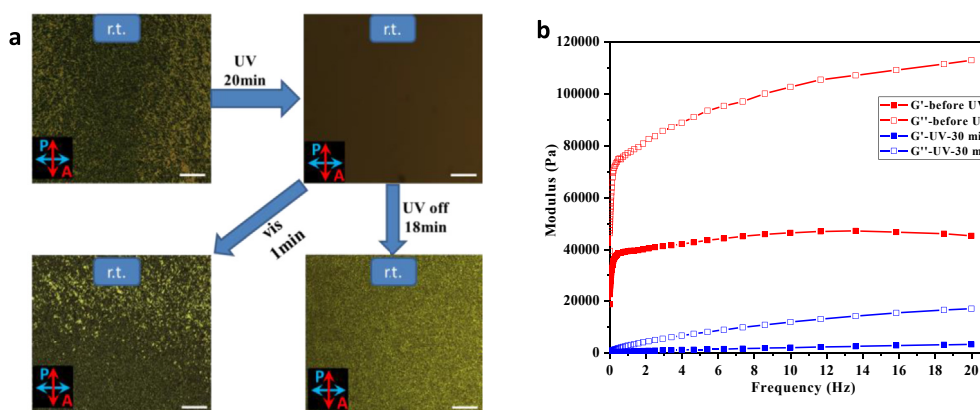


Fig. 4. (a) Photoinduced phase transitions of DNA-1-DOAB (1:3:2) at r.t. The scale bar is 50  $\mu$ m. (b) Rheological analysis on storage ( $G'$ ) and loss ( $G''$ ) moduli as a function of the shear frequency of DNA-1-DOAB (1:3:2) before (red curves) and after (blue curves) UV illumination at r.t.

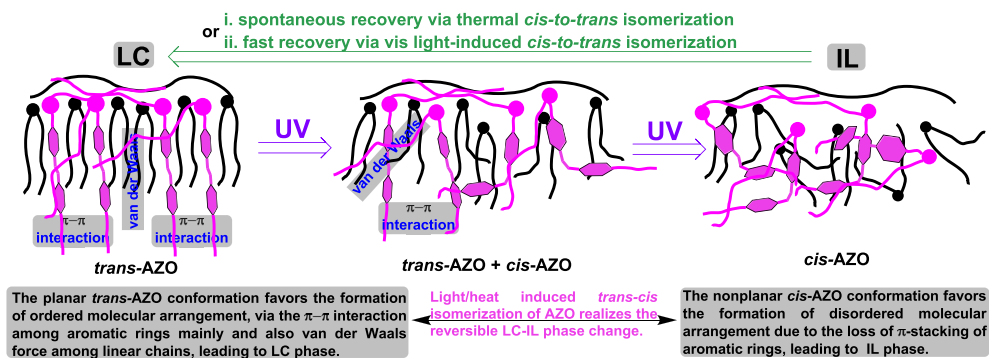


Fig. 5. A mechanism explanation on the photoresponsive isothermal LC  $\rightleftharpoons$  IL transition of DNA-1-DOAB TLCs.

for the photoisomerization of **1** by forming appropriate packing density, thanks to the breaking effect of DOAB to the  $\pi$ - $\pi$  interaction among **1**. Under UV light, the *trans*  $\rightarrow$  *cis* isomerization results in the formation of nonplanar conformation of **1**, which disorganizes the arrangement of surfactants to a loose packing density. The loose packing density would promote the UV light penetration into materials, facilitating the *trans*  $\rightarrow$  *cis* isomerization process of **1** until the complete formation of IL state. Compared to DNA-1-DOAB (1:3:2), DNA-1 (1:5) and DNA-1-DOAB (1:4:1) get a much higher packing density of surfactants because of the use of more amount of **1**, leading to no phase transition under UV light at r.t. An increased temperature would accelerate the molecular motion. As a result, sufficient free room for AZO isomerization could be provided at a 'melted' state of the DNA materials, furnishing the formation of DNA-1 (1:5) and DNA-1-DOAB (1:4:1) ILs under UV light. The ILs of DNA-1 (1:5), DNA-1-DOAB (1:4:1), and DNA-1-DOAB (1:3:2) could revert back to the ordered LC phase via either slowly thermal *cis*  $\rightarrow$  *trans* isomerization without vis light or rapidly photoinduced *cis*  $\rightarrow$  *trans* isomerization with vis light. As for DNA-1-DOAB (1:2:3) and DNA-1-DOAB (1:1:4), less use of functional

photochromic molecules makes the reversible isothermal phase transition impossible.

### 3.6. Shape information recording and self-erasing tests

The fabricated soft DNA TLCs would be attractive information storage biomaterials with the self-erasing property. A practical test on this topic was carried out with DNA-1-DOAB (1:3:2), based on its photoinduced isothermal phase transition ability at r.t. As shown in Figs. 6 and S8, the pristine DNA TLC showing smooth morphology on the top surface could be easily marked by the Roman number I, which indicates the good processability of the fabricated biomaterial. After 20 min UV illumination, the number I was erased due to the LC  $\rightarrow$  IL phase change, and the LC state of DNA-1-DOAB (1:3:2) was recovered within 30 min after ceasing UV light. Repeatable information input by marking Roman numbers II and III and following self-erasing under UV light confirmed the reworkable property of this DNA TLC. Interestingly, this DNA TLC also exhibits good shape memory property, proved by an overnight information storage test with the number III state. The processability, shape

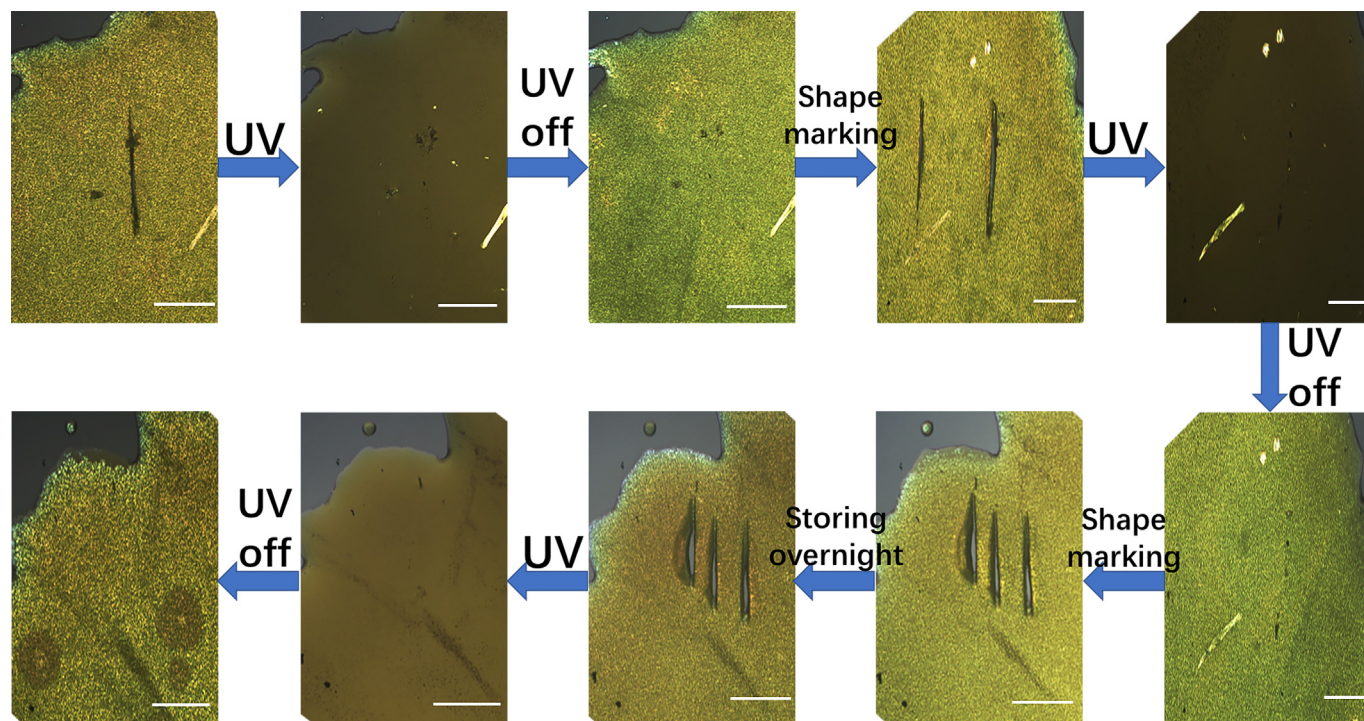


Fig. 6. The information input, self-erasing, and shape memory tests with sample DNA-1-DOAB (1:3:2) TLC. The scale bar is 100  $\mu$ m. All the images have been clipped on the size and adjusted on the resolution for a better view. The original files are put in Fig. S8. UV irradiation times range from 30 min to 50 min depending on the marking depth, and UV off times are 30–60 min for a full recovery of the LC state.

memory, and self-erasing properties would make the reported soft DNA materials be useful information storage biomaterials. It is worth noting that this kind of DNA TLCs exhibits good ‘rigidity’ for the shape information recording and holding the information integrity under external force, which is evidenced by this shape information writing/memory test (Fig. 6) and the dynamic mechanical analysis (Fig. 4b).

#### 4. Conclusion

In this study, a new type of AZO-containing surfactant **1** with good water solubility and flexibility was designed and synthesized for the fabrication of solvent-free soft DNA materials with photoresponsive properties at r.t. The *trans* ⇌ *cis* photoisomerization of **1** could effectively regulate the isothermal phase transitions and mechanical properties of the fabricated DNA materials at temperatures below their clearing points. The composition of applied surfactants of **1** and DOAB has a great impact on the required temperature condition for furnishing the process of isothermal phase crossover. The developed phase change DNA materials at or near r.t. would be good biomaterials with potential applications in various areas. For example, these DNA materials could be applicable as erasable information tags for recording important messages during the use of perishable medical products. This study also provides a strategy for designing soft anhydrous biomaterials with effective photoregulated phase change properties at different temperature conditions below the clearing point.

#### Credit author statement

Lei Zhang: Conceptualization, Investigation, Formal analysis; Yang Qu: Investigation; Jingjing Gu: Investigation; Yun Liu: Investigation; Zhenyu Tang: Investigation; Chenghao Zhang: Investigation; Han Liu: Investigation; Jishuai Liu: Investigation; Zhongtao Wu: Conceptualization, Methodology, Writing – original draft; Xiliang Luo: Supervision, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mtbio.2021.100140>.

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