NIR-Light-Induced Deformation of Cross-Linked Liquid-Crystal Polymers Using Upconversion Nanophosphors

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S *Supporting Information*

ABSTRACT: When upconversion nanophosphors were incorporated into an azotolane-containing cross-linked liquid-crystal polymer film, the resulting composite film generated fast bending upon exposure to continuous-wave near-IR light at 980 nm. This occurs because the upconversion luminescence of the nanophosphors leads to trans—cis photoisomerization of the azotolane units and an alignment change of the mesogens. The bent film completely reverted to the initial flat state after the light source was removed.

Light-driven organic actuators have received significant attention in recent years because they can convert light energy directly into mechanical work and act by remote, instant, and precise control. Several types of photosensitive polymers have been developed as organic actuator materials, including gels,[1] shape-memory polymers,[2] and cross-linked liquid-crystal polymers (CLCPs).[3] As a combination of polymer networks and liquid crystals (LCs), CLCPs exhibit such unique properties as elasticity, anisotropy, stimulus-responsiveness, and molecular-cooperation effects. Especially, it has been reported that CLCPs undergo large thermal-induced contractions due to changes in the molecular alignment of mesogens caused by the thermal phase transition from the LC to an isotropic state.[4] Furthermore, several good methods have been developed to incorporate widely used photochromic molecules such as azobenzenes into the side chains of polymer networks to achieve photoresponsive CLCPs, in which the azobenzene units are able to act as mesogens. The cooperative motion of LC molecules is then utilized to magnify the microscopic structural change in the azobenzene units and the alignment change of the mesogens induced by UV light into significant macroscopic photodeformations of the whole material, such as contraction,[5] bending,[6] rotation,[7] swimming,[8] cilia motion,[9] inchwormlike walking, and arm-mimic motion.[10] Furthermore, full-light-driven oscillators,[11] microrobots,[12] micropumps,[13] and microvalves[14] based on photodeformable CLCPs have been fabricated. Recently, azotolane-containing CLCPs have been prepared whose deformation can be induced by visible light and even by direct sunlight as a result of the enlarged conjugation structure of the azotolane units.[15]

To develop applications of light-driven organic actuators in possible biological systems, low-energy light (e.g., NIR light) instead of UV or visible light would be a more suitable stimulating source because low-energy light penetrates deeper into tissues and causes less damage to biosamples. There have been several examples in which NIR light was used to control the actuation process of CLCPs.[16] In these cases, NIR-light-induced thermal effects were utilized, and thermal conduction materials such as carbon nanotubes (CNTs) were incorporated into thermoresponsive CLCPs. Because CNTs absorb and transform NIR light energy into thermal energy, they serve as a nanoscale heat source to induce the LC—isotropic thermal phase transition and thus the contraction of the thermoresponsive CLCPs. In our work, upconversion nanophosphors (UCNPs) were incorporated into the photoresponsive CLCPs as antennae species that absorb continuous-wave (CW) NIR light and transfer the available energy to the photochromic units. The resulting composite films generated photodeformation upon irradiation with NIR light, which is obviously different from the actuation principle of the thermoresponsive CLCPs by NIR light.

UCNPs consisting of certain lanthanide dopants embedded in a nanocrystalline host lattice can convert CW NIR light into emission at UV and visible wavelengths via the sequential absorption of two or more low-energy photons.[17] It has been reported that dithienylethene[18] photoswitches undergo their ring-closing and ring-opening reactions when triggered by NIR light in the presence of two types of UCNPs that emit UV and visible light.[19] However, photochromic azo systems incorporating UCNPs have not been reported. Herein we report for the first time that with the help of the upconversion luminescence (UCL) of UCNPs, trans—cis photoisomerization of azo compounds can be induced upon exposure to CW NIR light, leading to the CW NIR-light-induced deformation of the CLCP/UCNP composite films.

In our design strategy, we chose UCNPs composed of $NaYF_4$: 20 mol%Yb^{3+}, 1 mol%Tm^{3+} to combine the azotolane CLCP into one composite film, because Tm^{3+}-doping UCNPs show UCL emission at 350-475 nm which matches the absorption band of the azotolane CLCP (Figure 1a) prepared from LC compounds **1** and **2** (Scheme 1a). We expect that energy transfer from UCL of UCNPs to the absorption of the azotolane CLCP happens.

UCNPs were synthesized according to a modified literature procedure[20] and characterized by transmission electron microscopy (TEM) and power X-ray diffraction (XRD) analysis. The TEM image of the as-prepared UCNPs clearly shows uniform nanocrystals with an average diameter of ~70 nm (Figure 1b). From the powder XRD pattern [Figure S1 in the Supporting Information (SI)], it can be seen that the nanocrystals display a hexagonal phase of $NaYF_4$, which was further confirmed by the observation of the lattice distances of 0.52 nm in the high-resolution TEM (HRTEM) image (Figure 1c). The energy-dispersive X-ray analysis pattern indicates the presence of Na, Y, Yb, and F in the UCNPs (Figure S2).

As shown in Figure 1a, under excitation with a 980 nm CW laser, the as-prepared UCNPs show blue emission (Figure 1a inset)
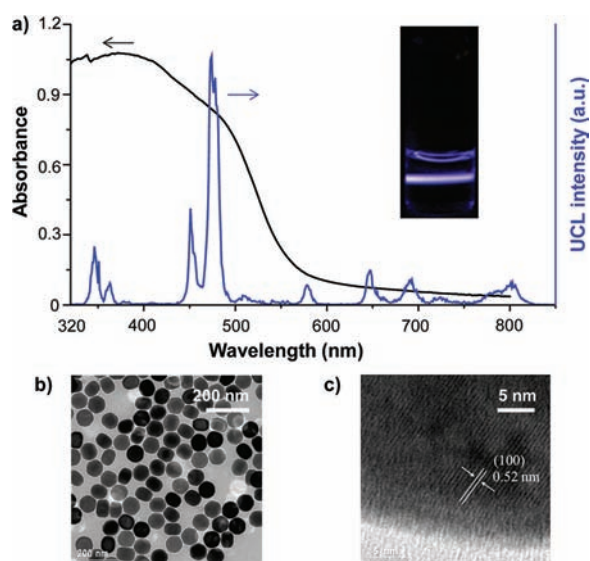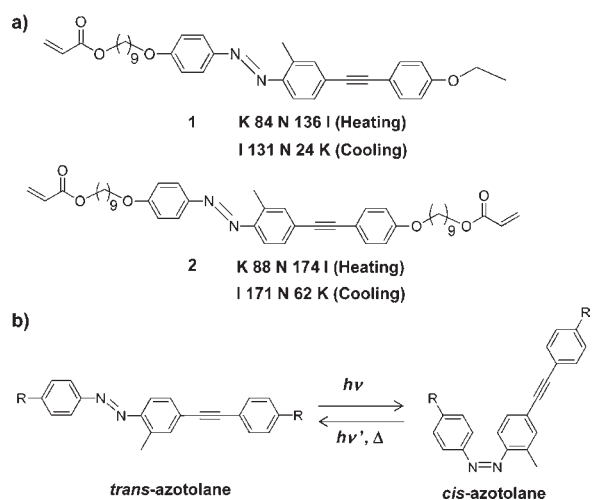
Figure 1. (a) UCL emission spectrum (blue line) of a colloidal $CHCl_3$ solution of UCNPs (1 mg/mL) excited with a 980 nm CW laser (power = 600 mW, power density =15 W/cm^2) and the UV−vis absorption spectrum (black line) of the azotalane CLCP film prepared according to the reported procedure.[15] The inset shows a photograph of UCL from the UCNPs in $CHCl_3$. (b) TEM and (c) HRTEM photographs of the as-prepared UCNPs.

Scheme 1. (a) Chemical Structures and Properties of Azotolane-Containing LC Compounds 1 and 2 Used in This Study (K, Crystal; N, Nematic; I, Isotropic) and (b) Photoisomerization of the Azotolane Unit

Figure 2. (a) Changes in UCL emission spectra of a colloidal $CHCl_3$ solution of UCNPs upon addition of different concentrations of the mixture of LC compounds **1** and **2** under CW excitation at 980 nm (power density = 15 W/cm^2). The molar ratio of **1** to **2** was 4:6, and the weight ratio of UCNPs to LC compounds was 1:0, 1:0.5, 1:1, 1:1.5, or 1:2. (b) Changes in the absorption spectrum of the $CHCl_3$ solution of LC compound **1** in the presence of UCNPs upon irradiation with CW 980 nm light (power density = 15 W/cm^2) for different times. [**1**] = 0.8×10^{-5} mol/L; [UCNPs] = 0.2 mg/mL.

and UCL emission peaks mainly located at 350, 365, 450, and 475 nm, corresponding to the $^3P_0 \rightarrow {}^3F_4$, $^1D_2 \rightarrow {}^3H_6$, $^1D_2 \rightarrow {}^3F_4$, and $^1G_4 \rightarrow {}^3H_6$ transitions, respectively. Also, relatively weak UCL emissions from 580 to 800 nm were observed. On the other hand, the azotolane CLCP film exhibits a broad and strong absorption band between 320 and 550 nm (Figure 1a). It is noted that the main UCL emission peaks of the UCNPs at 450 and 475 nm (their integral counts as >58%) overlap the absorption band of the azotolane CLCP film perfectly, making it possible for the UCL light emitted by the UCNPs to trigger the trans−cis photoisomerization of the azotolane moieties (Scheme 1b).
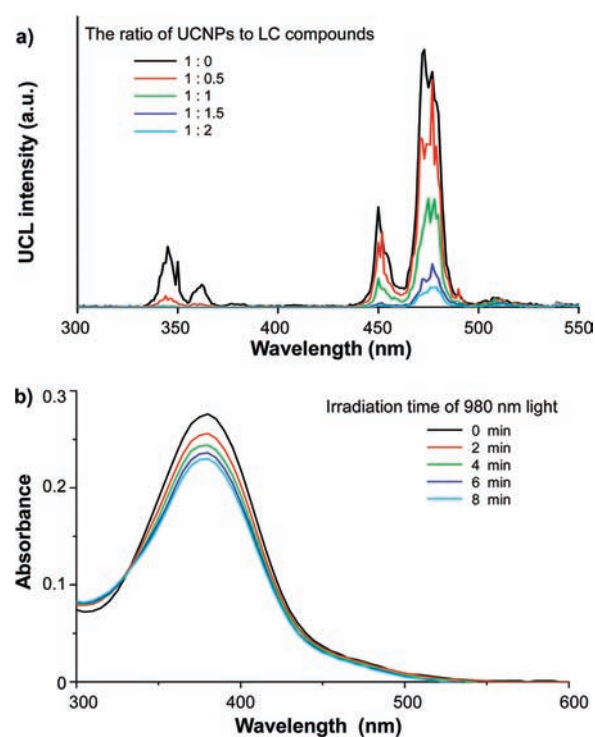
Figure 2a shows the changes in the UCL emission spectra of the colloidal $CHCl_3$ solution of UCNPs upon addition of different concentrations of the LC compounds **1** and **2** (Scheme 1a). The molar ratio of **1** to **2** added in the solution was 4:6, which agrees with that used to prepare the CLCP films. It is clear that the UCL intensities of the UCNPs at 350, 365, 450, and 475 nm decrease significantly with an increase in the proportion of the azotolane compounds, indicating that the UCL emission is effectively quenched by the azotolane compounds through the emission−reabsorption process and intermolecular energy transfer[21] from the UCNPs to the azotolane units. Additionally, Figure 2b shows the changes in the absorption spectra of a $CHCl_3$ solution of LC compound **1** in the presence of UCNPs upon exposure to CW 980 nm light for different times. With increasing irradiation time, the absorbance of the maximal absorption band at 385 nm of **1** obviously decreases. These results confirm that the UV and visible UCL light from UCNPs can cause the trans−cis photoisomerization of the azotolane units in the LC compounds (Scheme 1b).

Furthermore, UV−vis absorption spectra of the azotolane CLCP film were measured upon irradiation with visible light at 470 nm obtained from a light-emitting diode irradiator. As shown in Figure S3, the absorbance decreased gradually with increasing irradiation time as a result of the trans−cis photoisomerization of the azotolane units in the CLCP film.[15] This fact also supports the above-mentioned deduction that the UCL emission of UCNPs is able to induce the trans−cis photoisomerization of the azotolane
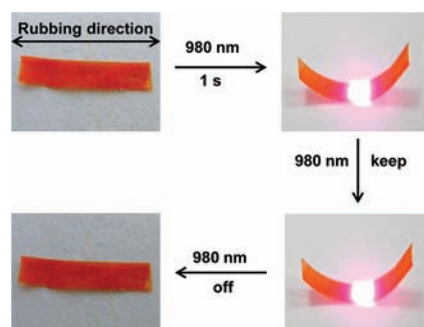
Figure 3. Photographs of the azotolane CLCP/UCNP composite film bending toward the light source along the alignment direction of the mesogens, remaining bent in response to the CW NIR irradiation at 980 nm (power density = 15 W/cm^2), and becoming flat again after the light source was removed. The size of the composite film was 8 mm × 2 mm × 20 μm.

units in the CLCP film (Scheme 1b), since the absorption band of the azotolane CLCP film covers the UV and visible UCL regions of the UCNPs (Figure 1a).

The CLCP/UCNP composite film was prepared by coating UCNPs on the surface of the azotolane CLCP film. Polarizing optical micrographs of the composite film (Figure S4) revealed that the azotolane mesogens are preferentially aligned along the rubbing direction without the effect of the coating treatment. The CW NIR-light-induced deformation of the CLCP/UCNP composite film is demonstrated in Figure 3. When irradiated with CW 980 nm light, the composite film bent toward the light source along the alignment direction of the mesogens within 1 s, which is ascribed to the trans—cis photoisomerization of the azotolane units (Scheme 1b) and the subsequent alignment change of the mesogens in the CLCP film induced by the UV and visible UCL emission of the UCNPs. Moreover, the bent film quickly reverted to the initial flat state when the CW 980 nm irradiation was removed. In order to recognize the trans—cis photoisomerization being transferred to the bending motion directly, experimental data concerning the anisotropic effect of the azotolane mesogens on the deformation were obtained (Figure S5). It was found that the square-shaped monodomain composite film bent along the rubbing direction of the polyimide alignment layers (Figure S5a), whereas the bending direction of the square-shaped polydomain composite film was random (Figure S5b) because of its inhomogeneous alignment of the mesogens on the macroscopic scale.

For comparison, a blank azotolane CLCP film without the UCNP coating was also irradiated with CW 980 nm light. However, it remained in the flat state, showing only a little thermal expansion in the irradiated region (Figure 4a) as a result of the thermal effect of NIR light, which produced a maximum temperature of up to 32 °C as measured by a thermal imager (Figure S6a). This demonstrates that the introduction of UCNPs is required to achieve the CW NIR-light-induced bending of the azotolane CLCP film. In addition, the bending of the CLCP/UCNP composite film does not arise from thermal contraction[4] in the surface region due to the LC—isotropic thermal phase transition.

Another contrast test showed that to realize the NIR-light-induced deformation of CLCPs, it was important to choose the azotolane CLCPs instead of the usual azobenzene ones, because the azotolane CLCPs display a red shift in the absorption band that significantly matches the main UCL emission of the UCNPs at 450 and 475 nm (Figure 1a), in comparison with the maximal absorption peak at 360 nm for the azobenzene CLCPs. As shown
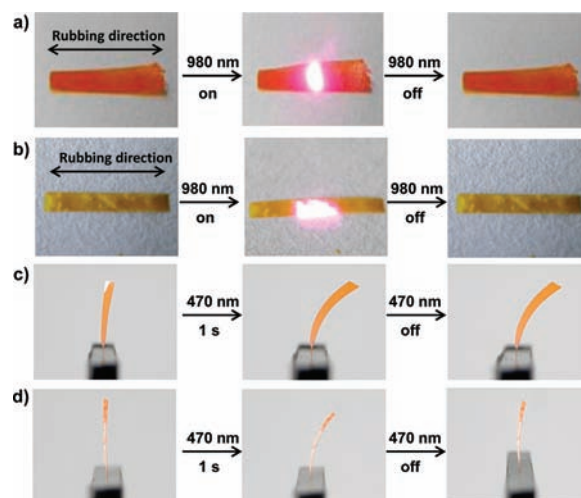

Figure 4. (a, b) Photographs of (a) the blank azotolane CLCP film without the UCNP coating and (b) the azobenzene CLCP/UCNP composite film upon irradiation with CW 980 nm light (power density = 15 W/cm^2) and after the irradiation was removed. (c, d) Photographs of (c) the blank azotolane CLCP film without the UCNP coating and (d) the azotolane CLCP/UCNP composite film upon irradiation with 470 nm light (25 mW/cm^2) and after the irradiation was removed. The size of the films was about 8 mm × 2 mm × 20 μm.

in Figure 4b, upon irradiation with CW NIR light at 980 nm, the azobenzene CLCP/UCNP composite film remained unbent, exhibiting only a little thermal expansion. It was observed that the azobenzene CLCP film generated bending upon irradiation with 365 nm light due to the trans—cis isomerization of azobenzene[6] and that the bent film recovered to the initial flat state when exposed to 470 nm light as a result of the cis—trans back-isomerization of azobenzene (Figure S7). For the azobenzene CLCP/UCNP composite film, the UCL emission peaks at 450 and 475 nm (integral counts as >58%) are higher than those at 350 and 365 nm (integral counts as >10%), so the cis—trans back-isomerization of azobenzene predominates under irradiation with NIR light (Figure S8). This explains the observation that the azobenzene-CLCP/UCNP film remained unbent upon irradiation at 980 nm (Figure 4b) and indicates that the choice of the azotolane CLCP rather than the azobenzene CLCP is judicious for realizing NIR-light-induced deformation of CLCPs by coating with a layer of UCNPs.

Furthermore, the NIR-light-induced thermal effect of the azotolane CLCP/UCNPs composite film was determined using the thermal imager. It was observed that the maximum temperature of the azotolane CLCP/UCNPs composite film reached 35 °C under irradiation with CW 980 nm light (15 W/cm^2) for 2.7 s (Figure S6b). This thermal effect of NIR light leads a small portion of the azotolane units to undergo the cis—trans back-isomerization,[22] which gives rise to a little recovery of the bent CLCP/UCNP composite film to the initial flat state when the irradiation with CW 980 nm light is removed (Figure 3). Besides the thermal-induced restoration, we deduce that the layer of UCNPs with a high stiffness is a main factor contributing to the recovery of the bent composite film.

To verify our deduction, a control experiment was designed to investigate the photodeformation of the azotolane CLCP/UCNP composite film and the blank azotolane CLCP film upon irradiation with 470 nm light instead of CW 980 nm light. It was observed that both of the films bent rapidly upon exposure to 470 nm light (Figure 4c,d). After the irradiation was removed, the blank CLCP

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film remained bent (Figure 4c), whereas the bent composite film reverted quickly to the initial flat state (Figure 4d). The introduction of UCNPs brings about a significant increase in the rigidity of the composite film. This control experiment indicates that the recovery of the bent composite film shown in Figure 3 after removal of the irradiation with 980 nm light is principally due to the effect of the rigid UCNP layer.

In addition, it was observed that the bending of the azotolane CLCP/UCNP composite film was kept during continuous irradiation of CW 980 nm light (Figure 3a) because the photoinduced trans—cis isomerization of the azotolane moieties generates a continuous stress that contributes to the bending of the film. Moreover, the bending and unbending of the composite film was performed for several reversible cycles when the NIR light was switched on and off repeatedly (see the movie in the SI).

In summary, by combination of an azotolane-containing CLCP film and $NaYF_4$:Yb,Tm upconversion nanophosphors, the resulting CLCP/UCNP composite film generated fast bending upon irradiation with CW NIR light at 980 nm. This shows that not only the photoisomerization of the chromophores but also the alignment change of the LC mesogens can be triggered by a judicious choice of the photochromic units in CLCPs and UCNPs. Significantly, the use of CW NIR light rather than light from a focused femtosecond NIR laser, which could induce the bending of molecular-crystal nanorods composed of 9-anthracene-carboxylic acid,[23] has such advantages as higher efficiency and lower power density. Thus, this kind of novel photodeformable CLCP system is promising for biological applications such as artificial musclelike actuators and all-optical switches.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Preparation and characterization of UCNPs, CLCP films, and CLCP/UCNP composite films and a movie showing the bending and unbending of a composite film when the NIR light was switched on and off. This material is available free of charge via the Internet at http://pubs.acs.org.

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