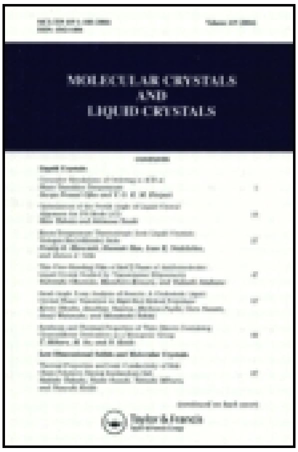

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NIR-Light-Driven Soft Actuation Materials Based on Crosslinked Liquid-Crystalline Polymers

Wei Wu [a] , Zhen Jiang [a] , Ruoyuan Yin [a] , Liming Yao [b] , Fuyou Li [b] & Yanlei Yu [a]

[a] Department of Materials Science, Fudan University, 220 Handan Road, Shanghai, 200433, China

[b] Department of Chemistry, Fudan University, 220 Handan Road, Shanghai, 200433, China

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NIR-Light-Driven Soft Actuation Materials Based on Crosslinked Liquid-Crystalline Polymers

WEI WU,[1] ZHEN JIANG,[1] RUOYUAN YIN,[1] LIMING YAO,[2]
FUYOU LI,[2] AND YANLEI YU[1,*]

[1]Department of Materials Science, [2]Department of Chemistry, Fudan University,
220 Handan Road, Shanghai 200433, China

Two kinds of composite films were obtained by incorporating upconversion nanophosphors into monodomain and polydomain crosslinked liquid crystalline polymer films containing azotolane moieties. When exposure to continuous-wave near-infrared light at 980 nm, the monodomain composite film generated fast bending along the rubbing direction of the polyimide alignment layers, whereas the bending direction of the polydomain composite film was random. The anisotropic effect of the azotolane mesogens on the deformation and the measurement of thermal effect indicate that the bending is caused by the means of photochemistry rather than the thermal effect of NIR light; that is, the upconversion luminescence of the nanophosphors leads to trans−cis photoisomerization of the azotolane units and the alignment change of the mesogens.

Keywords Deformation; light; liquid crystals; upconversion nanophosphors

1. Introduction

Soft actuation materials have experienced a vigorous development in recent years. They can undergo changes in shape due to a contractile or expanding force generated in response to physical or chemical stimuli, as the physical and chemical potential energy is able to be converted into mechanical work [1]. Among various stimulating sources, light arises more interest because it is a kind of clean energy which can be manipulated conveniently, precisely, instantly, and remotely. To perform a photomechanical effect, it is necessary for light-responsive polymers including photochromic moieties such as coumarin, spiropyran, stilbene, and azobenzene. As we all know, azobenzene has two different configurations, stable rod-like trans structure and metastable bent-shape cis isomer. Trans–cis and cis–trans isomerizations can be induced by alternate irradiation of UV and visible light [2].

With a combination of polymer networks and liquid crystals (LC), crosslinked LC polymers (CLCPs) exhibit such unique properties as elasticity, anisotropy, stimuli-responsiveness and molecular cooperation effect [3]. When azobenzene chromophores are incorporated into CLCPs, CLCPs show a large-scale photoinduced deformation upon irradiation with UV light, which is triggered by a microscopic change in the azobenzene

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[*] Address correspondence to Prof. Yanlei Yu, Department of Materials Science, Fudan University, 220 Handan Road, Shanghai 200433, China. Tel: (+86)21-55664576. Fax: (+86)21-55664576. E-mail: ylyu@fudan.edu.cn

structures through the cooperative movement of the LC mesogens and the polymer segments due to the domino effect [4]. It has been reported that the azobenzene-containing CLCP films generated a macroscopic contraction upon exposure to UV light, which is ascribed to the decrease in alignment order and eventually an LC–isotropic phase transition caused by the trans–cis photoisomerization of the azobenzene units in CLCPs [5]. Shortly afterwards, a bending deformation was successfully achieved by inducing an asymmetry contraction in the azobenzene CLCP films. When the azobenzene units are aligned into one direction in the monodomain CLCP films, the film surface contracts only in one direction upon the trans–cis photoisomerization and thus undergo an anisotropic bending with irradiation of UV light [6]. For the polydomain CLCP film, it consists of many micro-sized domains of the azobenzene mesogens aligned in one direction in each domain, although macroscopically the direction of alignment is random. On irradiation of the film with linearly polarized UV light, the selective absorption of light of a specific direction leads to the trans–cis isomerization of the azobenzene moieties in specific domains where the azobenzene moieties are aligned along the direction of light polarization. Therefore, the bending direction of the polydomain CLCP film can be precisely controlled by altering the direction of polarization of the irradiating light [7].

Recently, visible light and even sunlight were used as stimulating sources to induce bending deformation of the azotolane-containing CLCP films due to the enlarged conjugation structure of the azotolane units [8]. Moreover, many kinds of actuation movements based on above-mentioned CLCPs have been developed, such as a motor rotation [9], an inchworm walk [10], a robotic arm motion [10], swimming [11], and cilia motion [12]. Also, full-light-driven oscillators [13], microrobots [14], micropumps [15], and microvalves [16] have been successfully fabricated.

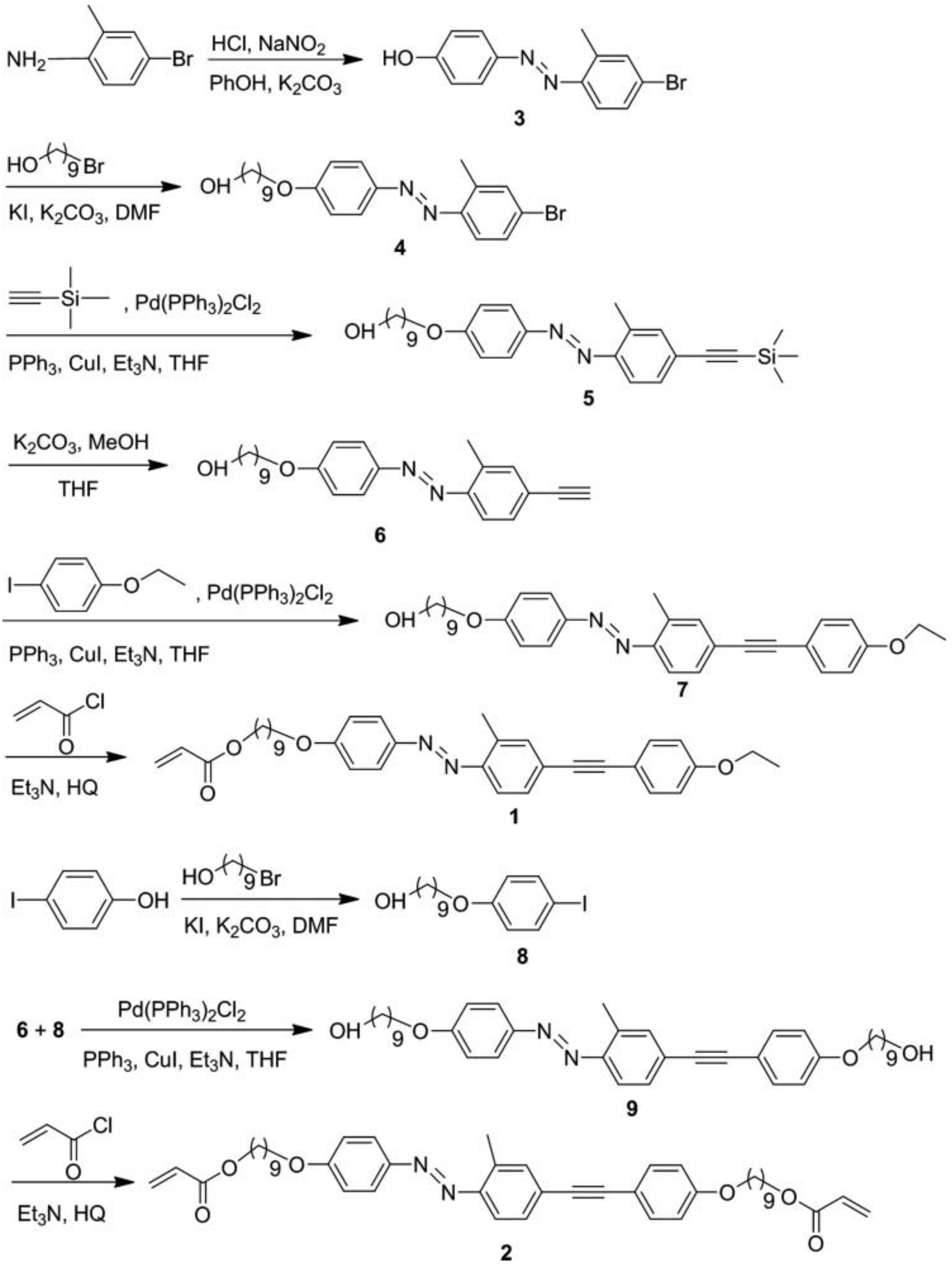
To extend the applications of soft actuation materials in biological environment, it is very significant to develop novel materials whose deformation is triggered by NIR light. Most recently, we reported that with combination of a monodomain azotolane-containing CLCP film and $NaYF_4$:Yb,Tm upconversion nanophosphors (UCNPs), the resulting CLCP/UCNP composite film generated fast bending along the alignment direction upon irradiation with continuous-wave (CW) NIR light at 980 nm [17]. In this paper, to further verify that the bending deformation of the CLCP/UCNP composite film is induced by the photochemical process, not only the monodomain composite film but also a polydomain composite film were prepared to investigate the mechanism of NIR-light-induced deformation. The anisotropic effect of the azotolane mesogens on the deformation of both films was observed to make clear the trans–cis photoisomerization being transferred to the bending motion directly.

2. Experimental

Materials

The LC compounds **1** and **2** were prepared according to our published work [8]. The synthetic routes of **1** and **2** are outlined in Scheme 1.

The azotolane CLCP films were prepared by copolymerization of the mixture of **1** and **2** with a molar ratio of 4:6 containing 4 mol% of a thermal initiator (2,2’-azobis(Ncyclohexyl-2-methylpropionamide), Wako Pure Chemical). The mixture and the initiator were injected into a glass cell at 120°C (a nematic phase) and the glass substrates were coated with polyimide alignment layers that had been rubbed to align the LC mesogens. The thermal



Scheme 1. Synthetic routes for compound **1** and **2**.

polymerization was carried out in a vacuum oven under nitrogen at 120°C for 24 h. The free-standing monodomain CLCP film was obtained by opening the cell and separating the film from the glass substrates. In addition, the polydomain azotolane CLCP film was prepared with the same process by injecting the polymerizable mixture into the glass cell whose polyimide layers had not been rubbed.

UCNPs composed of $NaYF_4$: 20 mol%Yb^{3+}, 1 mol%Tm^{3+} were synthesized according to a modified literature procedures [18]. YCl_3 (0.79 mmol), $YbCl_3$ (0.20 mmol), $TmCl_3$ (0.01 mmol) were added to a 100 mL three-neck round-bottom flask containing oleic acid (6 mL) and 1-octadecence (14 mL). The solution was stirred and heated to 150°C for 0.5 h to remove residual water. The temperature was then lowered to 50°C. A solution of sodium hydroxide (2.5 mmol) and ammonium fluoride (4 mmol) in methanol (8 mL) was added, and the solution was kept at 50°C for 0.5 h. The reaction mixture was then increased to 80°C to evaporate methanol from the reaction mixture. The reaction temperature was increased to 300°C under nitrogen for 1.5 h and cooled to room temperature. The nanoparticles were collected via centrifugation and washed several times with a mixture of cyclohexane and ethanol.

A solution of $NaYF_4$:Yb,Tm in hexane was then coated on the surface of the azotolane CLCP films. After the solvent volatilized, the CLCP/UCNPs composite films containing ~10 wt% of UCNPs were obtained.

Measurements

Energy-dispersive X-ray analysis (EDXA) of UCNPs was performed during transmission electron microscope (TEM; JEOL, JEM-2010F) measurements. X-ray diffraction measurement was made with an X-ray diffractometer (XRD; Bruker, D4) using Cu Kα radiation ($\lambda = 0.15406$ nm). Upconversion luminescence spectra were measured with a fluorescence spectrometer (Edinburgh, LFS-920) using an external continuous-wave (CW) 980 nm laser (Xi'an Saipulin Laser Technology Institute, China) with tunable power of 0–3 W as the excitation source, instead of the Xenon source in the spectrophotometer. The thermal effect of CW 980 nm light in the CLCP film was measured with thermal imagers (Mikron, M7500E and Fluke, Ti32). The optical anisotropy of the monodomain azotolane CLCP/UCNPs composite film was studied using a polarizing optical microscope (POM; Leika, DM2500p).

3. Results and Discussion

Structural Analysis of $NaYF_4$: 20 mol%Yb^{3+}, 1 mol%Tm^{3+} UCNPs

According to our reported work, the UCNPs showed uniform nanocrystals with an average diameter of ~70 nm from TEM image [17]. The XRD analysis of as-prepared UCNPs was performed. The powder XRD pattern (Fig. 1) shows 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 image [17]. In addition, the energy-dispersive X-ray analysis pattern indicates the presence of Na, Y, Yb, and F in UCNPs (Fig. 2).

Upconversion Luminescence Properties of $NaYF_4$: 20 mol%Yb^{3+}, 1 mol%Tm^{3+} UCNPs

Upconversion luminescence spectrum of the as-prepared UCNPs was shown in Fig. 3, under excitation with a CW 980 nm laser, the UCNPs shows the upconversion luminescence (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. Relative weak UCL emissions from 580 to 800 nm were also observed. According to our reported work

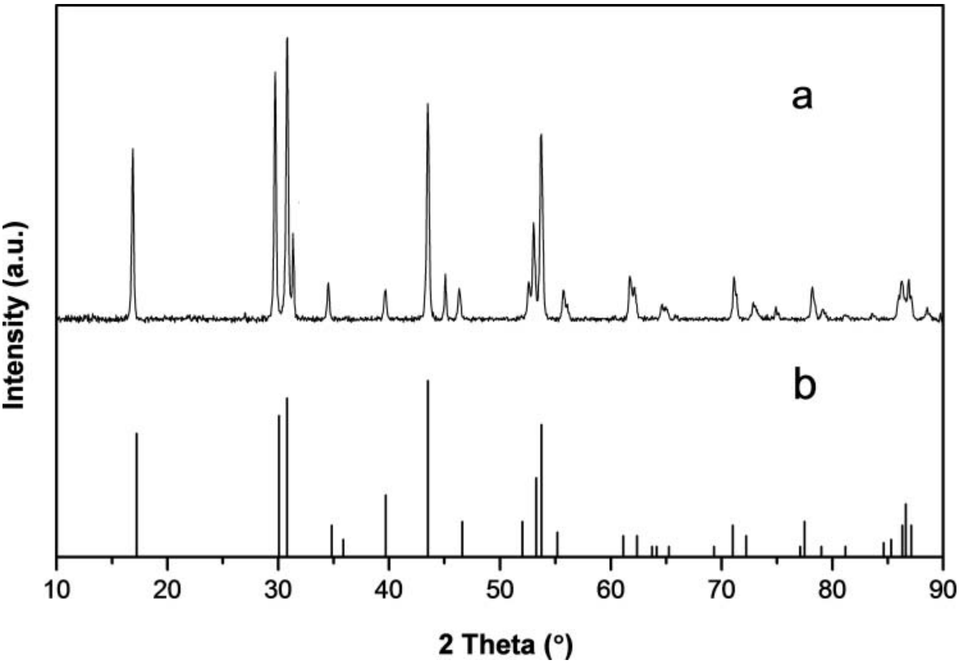


Figure 1. Powder XRD pattern for the as-prepared $NaYF_4$:Yb,Tm UCNPs (a) and $NaYF_4$ JCPDS standard card No.16-0334 (b).

[8, 17], the main UCL emission peaks at 450 and 475 nm (their integral counts $> 58\%$) of UCNPs overlap the absorption band of the azotolane CLCP film, which can be utilized to trigger the deformation of the azotolane CLCP films.

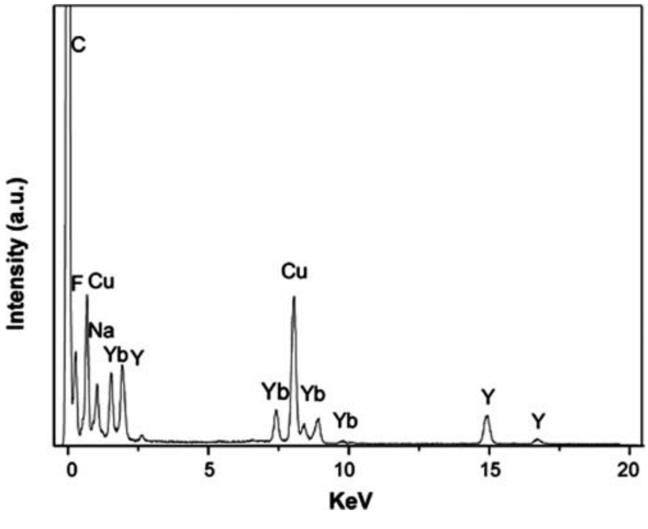


Figure 2. EDXA spectra of the as-prepared $NaYF_4$:Yb,Tm UCNPs.

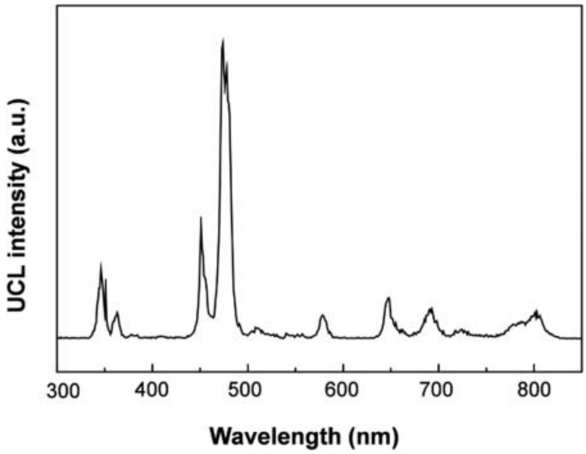


Figure 3. Upconversion luminescence spectrum of the colloidal $CHCl_3$ solution of UNCPs (1 mg/mL) excited with 980 nm CW laser (power = 600 mW, power density = 15 W/cm^2).

Optical Properties of the Azotolane CLCP Films and the Composite Films

To clarify the difference in optical properties of the as-prepared monodomain and polydomain azotolane CLCP films, their polarized absorption spectra were measured. In the monodomain film, $A_{//}$ and $A_{\perp}$ are the absorbance measured with light polarized parallel and perpendicular to the rubbing direction of the alignment layers, respectively. In the polydomain film, the polarization directions of measurement beam for A_0 and A_{90} were perpendicular to each other. As shown in Fig. 4, it is clear that the monodomain film showed high dichroism (Fig. 4(a)), while the polydomain film exhibited no dichroism (Fig. 4(b)).

Furthermore, the polarizing optical micrographs of the monodomain azotolane-CLCP/UCNPs composite film are shown in Fig. 5. The alignment of the azotolane mesogens in the composite films was evaluated at room temperature by measuring the transmittance of probe light through two crossed polarizers with a film between them. When the rubbing direction was parallel or perpendicular to the direction of polarizer of the microscope, no transmission light was observed, whereas the transmission was highest when the angle between them was 45°. Consequently, periodic changes of dark and bright images were observed by rotating the film with an interval of 45°. These results reveal that the azotolane mesogens are preferentially aligned along the rubbing direction without the effect of the coating treatment of the UCNPs layer.

In our recent work, we have confirmed that the UV and visible UCL light from UCNPs can induce the trans-cis photoisomerization of the azotolane units in the LC monomers used in this study [17]. Herein, the changes in UV-vis absorption spectra of the azotolane CLCP film were also measured upon irradiation with visible light at 470 nm obtained from a LED irradiator. As shown in Fig. 6, the absorbance decreased gradually with increasing irradiation time as a result of the trans−cis photoisomerization of the azotolane units in the CLCP film. Therefore, the UCL emission of UCNPs is possible to induce the trans−cis photoisomerization of the azotolane units in the CLCP film, since the absorption band of the azotolane CLCP film covers the UV and visible UCL regions of the UCNPs.

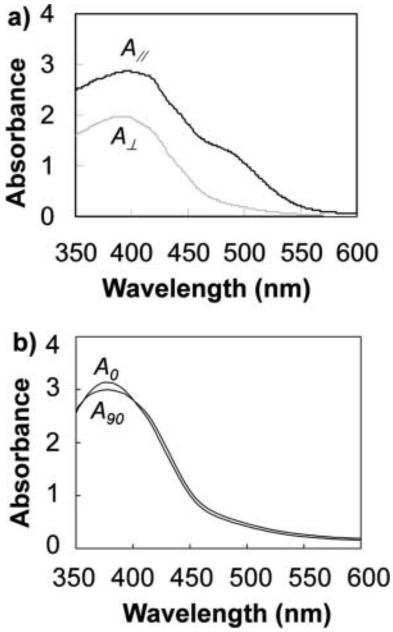


Figure 4. Polarized absorbance spectra of the monodomain azotolane CLCP film (a) and polydomain film (b). $A_{//}$ and $A_{\perp}$ are the absorbance measured with light polarized parallel and perpendicular to the rubbing direction of the alignment layers, respectively. The polarization directions of measurement beam for A_0 and A_{90} were perpendicular to each other. The thickness of the films is 2 μm.

Photoinduced Deformation of the Azotolane CLCP Films and the Composite Films

We first observed the photoinduced deformation of the as-prepared polydomain azotolane CLCP film when irradiated with visible light at 470 nm obtained from the LED irradiator. It

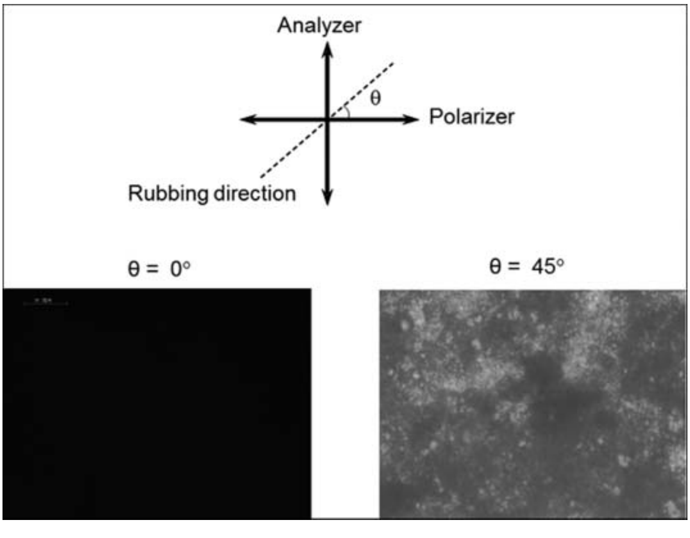


Figure 5. Polarizing optical micrographs of the azotolane CLCP/UCNPs composite film.

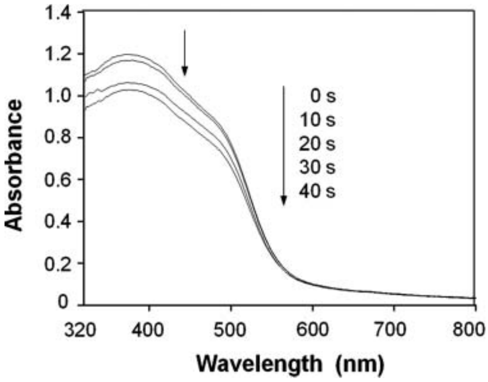


Figure 6. Change in the absorption spectra of the azotolane CLCP film (thickness: 2 μm) upon irradiation of visible light at 470 nm (3 mW/cm^2). The arrow shows the increment of irradiation time.

was found that the polydomain azotolane CLCP film generated the axis-selective photodeformation as the previously-reported polydomain azobenzene CLCP film [7]. As shown in Fig. 7, when irradiated with linearly polarized light at 470 nm, the bending direction of the polydomain azotolane CLCP film could be controlled by altering the direction of polarization of the incident light. It is because the direction of alignment of mesongens in the polydomain CLCP film is random macroscopically, at the same time, there were many

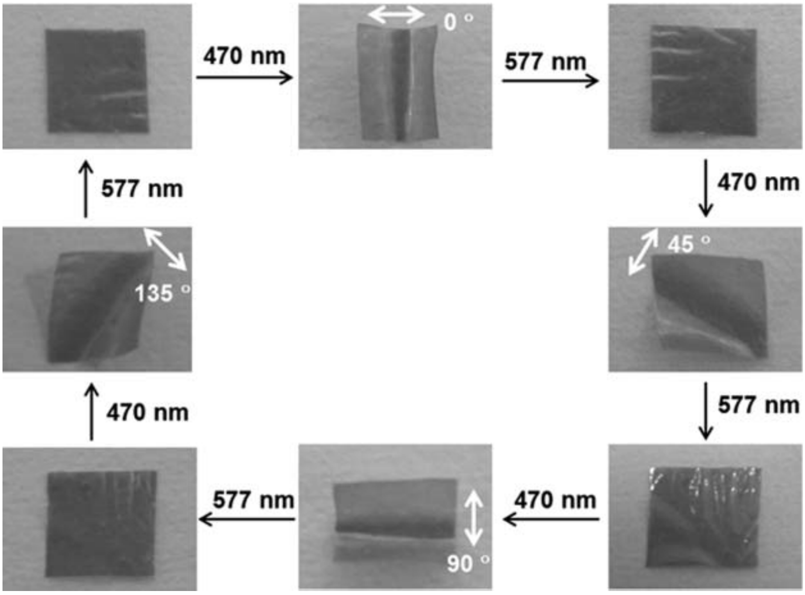


Figure 7. Photographic frames of the polydomain azotolane CLCP film bending in different directions in response to irradiation by linearly polarized light of different angles of polarization (white arrows) at 470 nm, and being flattened again by visible light at 577 nm. The light intensity of 470-nm and 577-nm linearly polarized light is 15 mW cm^{-2} and 30 mW cm^{-2}, respectively. The size of the film is 4 mm × 4 mm × 20 μm.

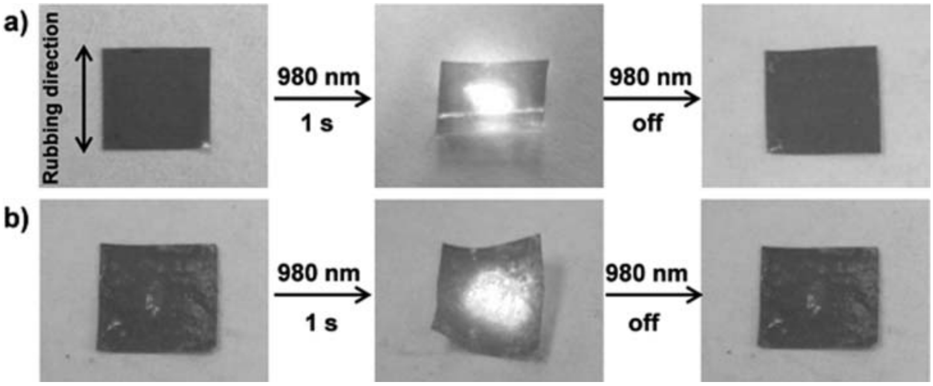


Figure 8. Photographic frames of the square-shaped azotolane-CLCP/UCNPs composite film: a) the monodomain film bent toward the light source along the rubbing direction of the polyimide alignment layers and the bent film reverted to the initial flat state after removing the light source; b) the bending direction of the square-shaped polydomain film is random due to its inhomogeneous alignment of the mesogens in the macroscopic scale. The irradiation source is NIR light at CW 980 nm (power density = 15 W/cm^2). The size of the composite films is 4 mm × 4 mm × 20 μm.

micro-sized domains aligned in one direction in each domain. Therefore, the selective absorption of light of a specific direction leads to a trans–cis isomerization of the azotolane moieties in specific domains where the azotolane moieties are aligned along the direction of light polarization.

Furthermore, the photoinduced deformation of the monodomain and polydomain azotolane-CLCP/UCNPs composite films was investigated when irradiated with CW 980 nm light. As Fig. 8(a) shows, the square-shaped monodomain composite film bent along the rubbing direction of the polyimide alignment layers. As the mesogens were aligned parallel to the rubbing direction of the polyimide alignment layers, the monodomain composite film bent only along this direction due to the trans−cis photoisomerization of azotolane units and the alignment change of the mesogens induced by the UCL emission of UCNPs. For the square-shaped polydomain composite film, the bending direction is random upon exposure to CW 980 nm light (Fig. 8(b)), because the mesongens are aligned randomly in the macroscopic scale. The anisotropic effect of the azotolane mesogens on the deformation indicates that the trans−cis photoisomerization of azotolane units is transferred to the bending motion directly; namely, the bending deformation of the composite films is induced by the photochemical process.

NIR-Light-Induced Thermal Effect in Azotolane-CLCP/UCNPs Composite Film

In order to further support that the bending deformation of the azotolane-CLCP/UCNPs composite films is induced by the photochemical process, we determined the NIR-light-induced thermal effect in the azotolane-CLCP/UCNPs composite film by 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 second (Fig. 9). When the irradiation was removed, the temperature went down rapidly to room temperature. Such small thermal effect is not able to induce a contraction in the CLCP films caused by LC-isotropic thermal phase transition.

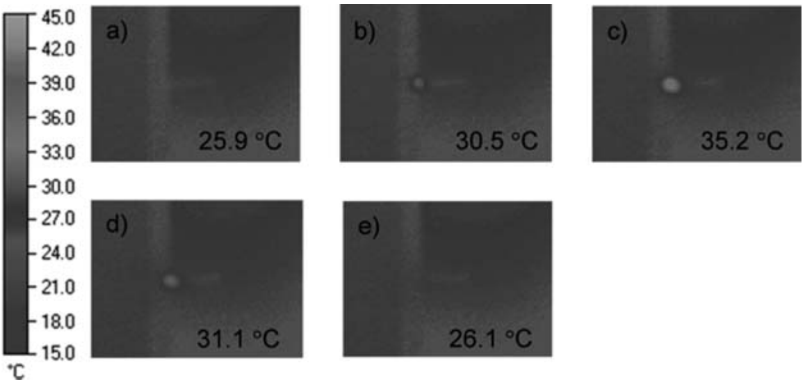


Figure 9. The thermal photographs of the azotolane CLCP/UCNPs composite film upon the irradiation of CW 980 nm light (power density = 15 W/cm^2) and after removing the light source when the environment temperature was 26°C: a) before irradiation, b) upon irradiation for 0.7 s, c) upon irradiation for 2.7 s, d) after removing the light source and keeping for 3.2 s, e) after removing the light source and keeping for 4.1 s. The size of the film is 8 mm × 2 mm × 20 μm.

According to the previous literature, NIR-light-induced thermal effect was used to control the actuation process of thermoresponsive CLCPs [19]. In these cases, CLCPs were incorporated with thermal conduction materials such as carbon nanotubes (CNTs) which absorbed and transformed NIR light energy into thermal energy. The thermal effect induced the LC-isotropic thermal phase transition and thus the contraction of the thermoresponsive CLCPs. However, this kind of reported actuation process is obviously different from the actuation principle of the azotolane-CLCP/UCNPs composite films investigated in our work. Therefore, it also indirectly indicates the bending of the composite film is caused by the trans-cis photoisomerization of the azotolane units rather than the thermal effect.

4. Conclusions

In conclusion, two kinds of CLCP/UCNPs composite films were prepared by incorporating the $NaYF_4$:Yb,Tm upconversion nanophosphors into the monodomain and polydomain azotolane-containing CLCP films. They generated the different bending deformations when irradiated with CW NIR light at 980 nm. The anisotropic effect of the azotolane mesogens on the deformation and the thermal effect measurement indicate that the bending is caused by the means of photochemistry rather than the thermal effect of NIR light. The novel photodeformable CLCP systems are promising for biological applications such as artificial muscle-like actuators and all-optical switches.

Acknowledgments

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References

[1] (a) Kuhn, W., Hargitay, B., Katchalsky, A., & Eisenberg, H. (1950). *Nature*, *165*, 514. (b) Steinberg, I. Z., Oplatka, A., & Katchalsky, A. (1966). *Nature*, *210*, 568. (c) Okuzaki, H., & Kunugi, T.

(1996). *J. Polym. Sci. Part B*, *34*, 1747. (d) Berna, J., Leigh, J., Lubomska, M., Mendoza, S. M., Perez, E. M., Rudolf, P., Teobaldi, G., & Zerbetto, F. (2005). *Nat. Mater.*, *4*, 704. (e) Eelkema, R., Pollard, M. M., Vicario, J., Katsonis, N., Ramon, B. S., Bastiaansen, C. W. M., Broer, D. J., & Feringa, B. L. (2006). *Nature*, *440*, 163.

[2] (a) Kupfer, J., Finkelmann, H., & Makromol, (1991). *Chem. Rapid Commun.*, *12*, 717. (b) Mol, G. N., Harris, K. D., Bastiaansen, C. W., & Broer, M. D. J. (2005). *Adv. Funct. Mater.*, *15*, 1155. (c) Li, M., Keller, P., Yang, J., & Albouy, P. (2004). *Adv. Mater.*, *16*, 1922. (d) Buguin, A., Li, M., Silberzan, P., Ladoux B., & Keller, P. (2006). *J. Am. Chem. Soc.*, *128*, 1088. (e) Yoshida, Y., Uchida, K., Kaneko, Y., Sakai, K., Kikuchi, A., Sakurai, Y., & Okano, T. (1995). *Nature*, *374*, 240. (f) Asoh, T., Matsusaki, M., Kaneko, T., & Akashi, M. (2008). *Adv. Mater.*, *20*, 2080.

[3] (a) de Gennes, P.-G., H_ebert, M., & Kant, R. (1997). *Macromol. Symp.*, *113*, 39. (b) Warner, M., & Terentjev, E. M. (2003). *Liquid Crystal Elastomers*, Oxford University Press, Oxford, UK. (c) Xie, P., & Zhang, R. (2005). *J. Mater. Chem.*, *15*, 2529.

[4] (a) Ikeda, T. (2003). *J. Mater. Chem.*, *13*, 2037. (b) Ikeda, T., Mamiya, J., & Yu, Y. (2007). *Angew. Chem., Int. Ed.*, *46*, 506.

[5] (a) Hogan, P. M., Tajbakhsh, A. R., & Terentjev, E. M. (2002). *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, *65*, 041720. (b) Li, M., Keller, P., Li, B., Wang, X., & Brunet, M. (2003). *Adv. Mater.*, *15*, 569. (c) Finkelmann, H., Nishikawa, E., Pereira, G. G., & Warner, M. (2001). *Phys. Rev. Lett.*, *8701*, 015501.

[6] (a) Yu, Y., Nakano, M., Shishido, A., Shiono, T., & Ikeda, T. (2004). *Chem. Mater.*, *16*, 1637. (b) Kondo, M., Yu, Y., & Ikeda, T. (2006). *Angew. Chem., Int. Ed.*, *45*, 1378. (c) Yu, Y., Maeda, T., Mamiya, J., & Ikeda, T. (2007). *Angew. Chem., Int. Ed.*, *4*, 881. (d) Zhang, Y., Xu, J., Cheng, F., Yin, R., Yen, C.-C., & Yu, Y. (2010). *J. Mater. Chem.*, *20*, 7123.

[7] Yu, Y., Nakano, M., & Ikeda, T. (2003). *Nature*, *425*, 145.

[8] (a) Yin, R., Xu, W., Kondo, M., Yen, C.-C., Mamiya, J., Ikeda, T., & Yu, Y. (2009). *J. Mater. Chem.*, *19*, 3141. (b) Cheng, F., Zhang, Y., Yin, R., & Yu, Y. (2010). *J. Mater. Chem.*, *20*, 4888.

[9] Yamada, M., Kondo, M., Mamiya, J., Yu, Y., Kinoshita, M., Barrett, C. J., & Ikeda, T. (2008). *Angew. Chem., Int. Ed.*, *47*, 4986.

[10] Yamada, M., Kondo, M., Miyasato, R., Naka, Y., Mamiya, J., Kinoshita, M., Shishido, A., Yu, Y., Barrett, C. J., & Ikeda, T. (2009). *J. Mater. Chem.*, *19*, 60.

[11] Camacho-Lopez, M., Finkelmann, H., Palffy-Muhoray, P., & Shelley, M. (2004). *Nat. Mater.*, *3*, 307.

[12] van Oosten, C. L., Bastiaansen, C. W. M., & Broer, D. J. (2009). *Nat. Mater.*, *8*, 677.

[13] (a) White, T. J., Tabiryan, N. V., Serak, S. V., Hrozhyk, U. A., Tondiglia, V. P., KWhite, T. J., Serak, S. V., Tabiryan, N. V., & Vaia, R. A. (2009). *J. Mater. Chem.*, *19*, 1080. (c) Serak, S., Tabiryan, N., Vergara, R., White, T. J., Vaia, R. A., & Bunning, T. J. (2010). *Soft Matter.*, *6*, 779.

[14] Cheng, F., Yin, R., Zhang, Y., Yen, C.-C., & Yu, Y. (2010). *Soft Matter.*, *6*, 3447.

[15] Chen, M., Xing, X., Liu, Z., Zhu, Y., Liu, H., Yu, Y., & Cheng, F. (2010). *Appl. Phys. A.*, *100*, 39.

[16] Chen, M., Huang, H., Zhu, Y., Liu, Z., Xing, X., Cheng, F., & Yu, Y. (2011). *Appl. Phys. A.*, *102*, 667.

[17] Wu, W., Yao, L., Yang, T., Yin, R., Li, F., & Yu, Y. (2011). *J. Am. Chem. Soc.*, *133*, 15810.

[18] (a) Qian, H.-S., & Zhang, Y. (2008). *Langmuir.*, *24*, 12123. (b) Cao, T., Yang, T., Gao, Y., Yang, Y., Hu, H., & Li, F. (2010). *Inorg. Chem. Commun.*, *13*, 392.

[19] (a) Koerner, H., Price, G., Pearce, N. A., Alexander, M., & Vaia, R. A. (2004). *Nat. Mater.*, *3*, 115. (b) Yang, L., Setyowati, K., Li, A., Gong, S., & Chen, J. (2008). *Adv. Mater.*, *20*, 2271.