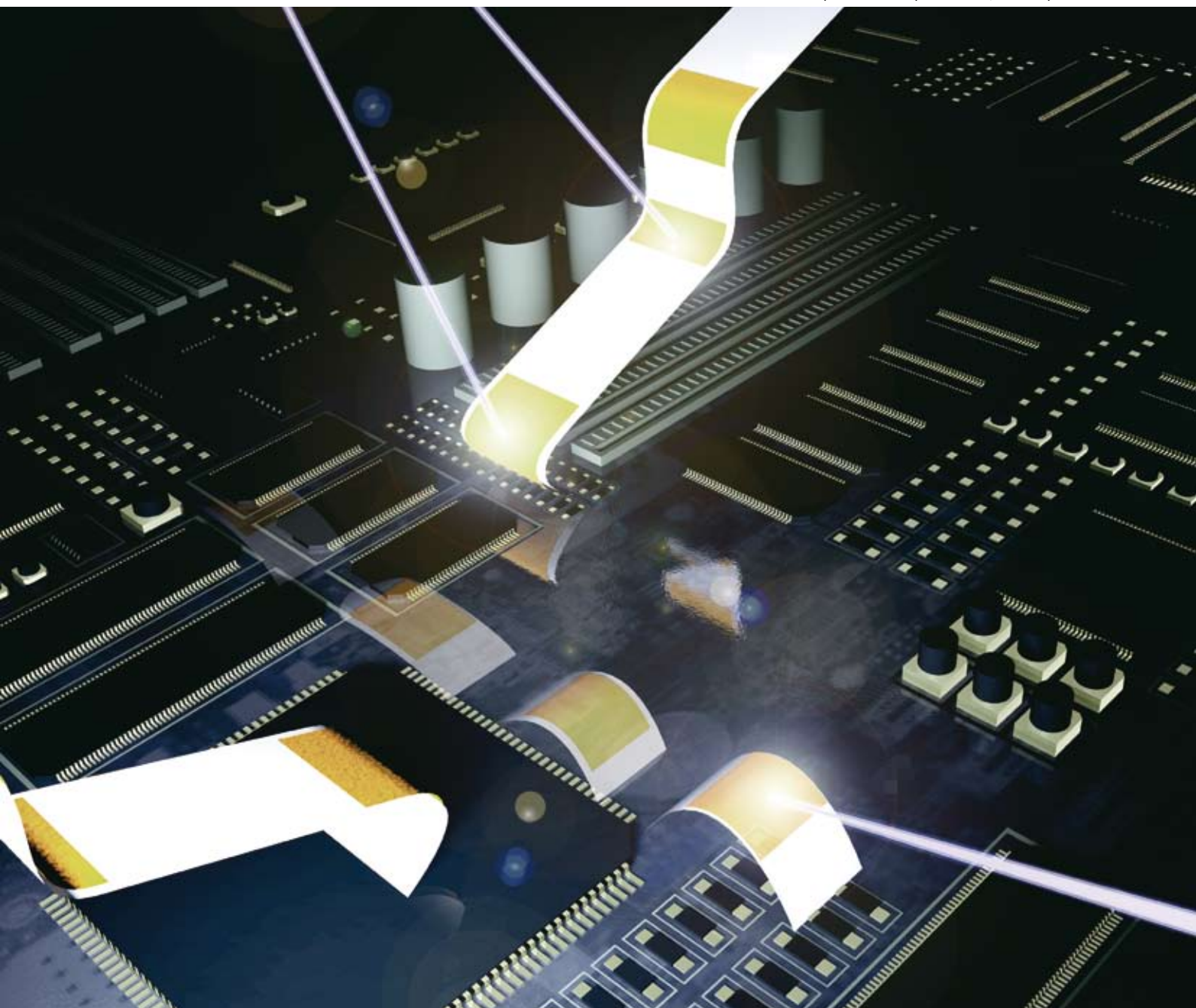


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Photomobile polymer materials—various three-dimensional movements†

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The composition of a crosslinked azobenzene liquid-crystalline polymer and a flexible polymer film can provide a variety of simple devices that can walk in one direction like an ‘inchworm’ and move like a ‘robotic arm’ induced by light.

Biomimetic actuators are receiving great interest for use as novel devices, such as humanoid robots and micro(nano)-machines, with stimulus-responsive gels and polymers.¹ In particular, soft materials driven by light could play an important role as efficient energy conversion systems because light is a good energy source that can be controlled remotely, instantly and precisely. Polymers incorporating photochromic molecules like an azobenzene, which photoisomerizes reversibly between a rod-like *trans* and a bent *cis* isomer upon irradiation, respond to light irradiation by either expanding or contracting by a few percent.²

Crosslinked liquid-crystalline polymers (CLCPs) are unique materials possessing the properties of both liquid crystals (LCs) and elastomers.^{3,4} CLCPs exhibit a contraction along the alignment direction of mesogens when heated above the LC–isotropic (I) phase transition temperature.⁵ By incorporating azobenzene moieties into CLCPs, a larger deformation can be induced by photochemical reactions of these azobenzene chromophores.⁶ Furthermore, bending of CLCP films composed only of azobenzene mesogens has been observed by irradiation with UV light.⁷ It has also been reported that some unique movements of CLCP films, such as oscillating, twisting and swimming, can be induced by light.⁸ Most recently, photoinduced rotational motions have been demonstrated, including a first light-driven plastic motor with CLCP laminated films.⁹

In this communication, we demonstrate new three-dimensional movements of architectures prepared from these photoresponsive materials. We were able to induce large and sophisticated motions of laminated films composed of a CLCP layer containing azobenzene moieties and a plastic sheet by photoirradiation, which leads to three-dimensional movements such as an inchworm walk and a flexible robotic arm motion.

Homogeneously aligned CLCP films used in this study were prepared by photopolymerization of a mixture of LC monomers (**1** and **2**) shown in Fig. 1a with a ratio of 20 : 80 mol : mol containing 2 mol% of a photoinitiator in a glass cell coated with rubbed polyimide alignment layers. The mixture shows a smectic phase on cooling from 89 °C, and photopolymerization was conducted at a temperature where the mixture exhibited a smectic phase. The freestanding CLCP films were taken off from the cells after polymerization. The CLCP films prepared in the smectic phase showed a higher order of azobenzene mesogens with their alignment along the rubbing direction of the polyimide alignment layers and produced a larger mechanical force by irradiation with UV light than those prepared in the nematic phase.⁷ Furthermore, the glass-transition temperature of the CLCP films appeared around room temperature as detected by differential scanning calorimetry, allowing the films to work at room temperature. The CLCP laminated films were prepared by thermal compression bonding of a CLCP layer and an unstretched low-density polyethylene (PE) film with an adhesion layer (Fig. 1b).

Fig. 2a shows a photoinduced motion of a CLCP laminated film having a curved shape, partly laminated with a CLCP layer. In this CLCP laminated film, the azobenzene mesogens were aligned

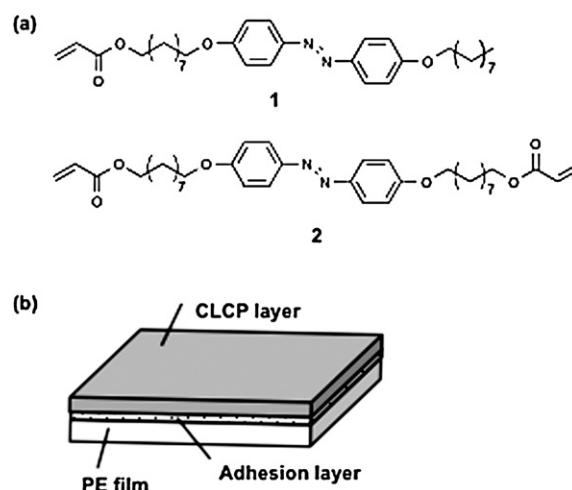


Fig. 1 Chemical structures of the LC monomer (molecule **1**) and LC diacrylate (molecule **2**) used in this study. On cooling from 92 °C, molecule **1** changes from an isotropic to a smectic phase, and at 60 °C it becomes crystalline; on cooling from 91 °C, molecule **2** changes from an isotropic to a smectic phase, and at 74 °C it becomes crystalline; on cooling from 89 °C, the mixture of molecule **1** + molecule **2** (20 : 80 mol : mol) changes from an isotropic to a smectic phase, and at 60 °C it becomes crystalline.

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† Electronic supplementary information (ESI) available: Synthesis and characterization details; movies showing inchworm walk and flexible robotic arm motions of CLCP laminated films. See DOI: 10.1039/b815289f

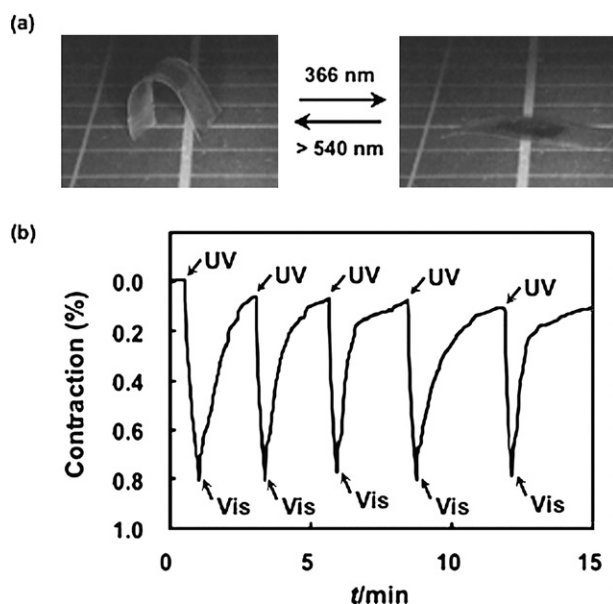


Fig. 2 (a) Photographs showing the photoinduced extension and retraction motion of the CLCP laminated film at room temperature. The film extended upon irradiation with UV light and reverted to the initial shape upon irradiation with visible light. Size of the CLCP laminated film: 16 mm $\times$ 8 mm; the CLCP laminated part: 6 mm $\times$ 5 mm. Thickness of the layers of the film: PE, 50 μ m; CLCP, 18 μ m. (b) Change in length of the CLCP layer by alternate irradiation with UV (366 nm, 20 mW cm⁻²) and visible light (>540 nm, 40 mW cm⁻²) at 30 $^{\circ}$ C.

along the long axis of the film. The CLCP laminated parts are curled due to the difference in the thermal expansion coefficients between the two layers. Upon irradiation with UV light, the laminated film extended to a flat shape and reverted to the initial bent shape upon irradiation with visible light, which could be repeated at room temperature just by changing the wavelength of the actinic light. We measured the change in length of the CLCP layer by alternate irradiation with UV and visible light (Fig. 2b). Upon exposure to UV light, the *trans-cis* photoisomerization of the azobenzene moieties in the CLCP layer occurs and a contraction force is generated along the alignment direction of the azobenzene mesogens of the CLCP layer through photoinduced reduction of LC order. The contraction of the CLCP layer results in extension of the whole laminated film. On the other hand, upon irradiation with visible light, the *cis-trans* back-isomerization occurs and the film reverts to the initial bent state.

Fig. 3a demonstrates a unidirectional motion, an inchworm walk, of the CLCP laminated film with asymmetric end shapes. The film moves forward upon alternate irradiation with UV and visible light at room temperature (see Movie 1 in the ESI† for real-time movement). A close inspection of this inchworm walk has revealed that upon exposure to UV light, the film extends forward because the sharp edge acts as a stationary point, and the film retracts from the rear side upon irradiation with visible light because the flat edge acts as the stationary point, which enables the film to move in one direction only (Fig. 3b).

Additionally, as CLCP laminated films are readily fabricated, we can easily make many devices in arbitrary shapes and sizes. In other words, we can make plastic films without photoresponsive

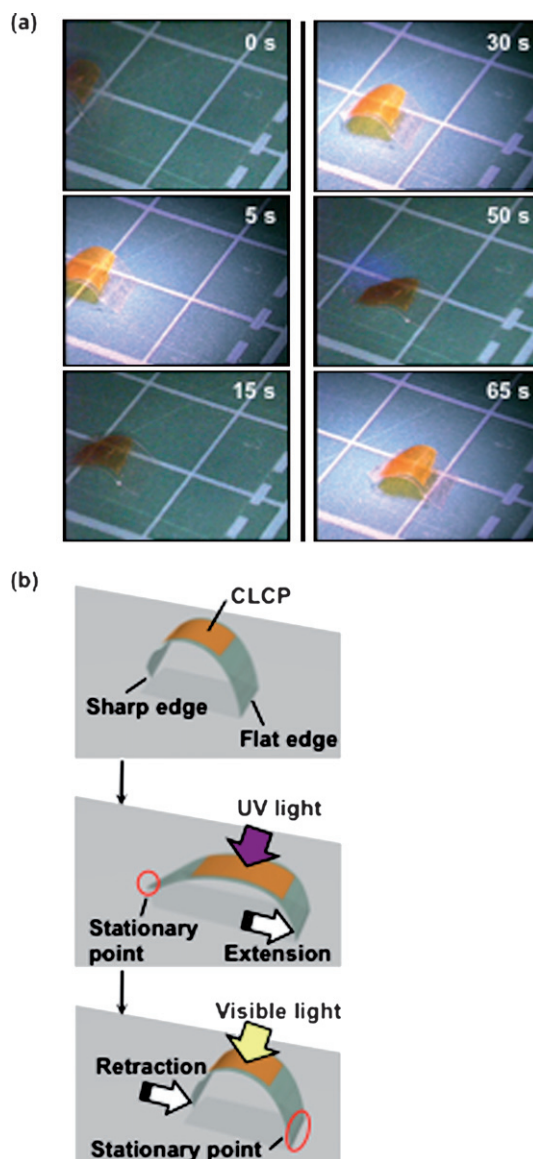


Fig. 3 (a) Series of photographs showing time profiles of the photoinduced inchworm walk of the CLCP laminated film by alternate irradiation with UV (366 nm, 240 mW cm⁻²) and visible light (>540 nm, 120 mW cm⁻²) at room temperature. The film moved on the plate with 1 cm $\times$ 1 cm grid. (b) Schematic illustrations showing a plausible mechanism of the photoinduced inchworm walk of the CLCP laminated film. Upon exposure to UV light, the film extends forward because the sharp edge acts as a stationary point (the second frame), and the film retracts from the rear side by irradiation with visible light because the flat edge acts as a stationary point (the third frame). Size of the film: 11 mm $\times$ 5 mm; the CLCP laminated part: 6 mm $\times$ 4 mm. Thickness of the layers of the film: PE, 50 μ m; CLCP, 18 μ m.

properties to move freely at any place by partially laminating with CLCP layers. For example, we prepared a rolled-up film by laminating with CLCP layers at two places as shown in the first frame of Fig. 4. The azobenzene mesogens here were aligned along the long axis of the film. Fig. 4 shows a sequential and flexible motion of the laminated film by light at room temperature (see Movie 2 in the ESI† for real-time movement). Upon exposure to UV light, the CLCP laminated parts extend from a curved shape

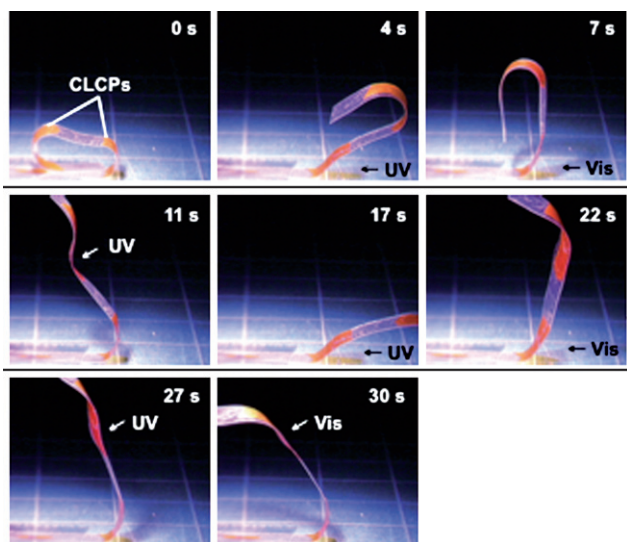


Fig. 4 Series of photographs showing time profiles of the flexible robotic arm motion of the CLCP laminated film induced by irradiation with UV (366 nm, 240 mW cm⁻²) and visible light (>540 nm, 120 mW cm⁻²) at room temperature. Arrows indicate the direction of light irradiation. Spot size of the UV light irradiation is about 60 mm². Size of the film: 34 mm × 4 mm; the CLCP laminated parts: 8 mm × 3 mm and 5 mm × 3 mm. Thickness of the layers of the film: PE, 50 μm; CLCP layers, 16 μm.

to a flat one and revert to the initial state upon irradiation with visible light, working as a 'hinge joint', which leads to a large and flexible movement of the whole film. By controlling the irradiation position and the intensity of the actinic light, one can drive the film in a chosen manner, which enables us to use it as a flexible 'robotic arm' to manipulate objects just by light irradiation.

In summary, laminated films composed of a homogeneously aligned CLCP layer and a PE film have been prepared. Large and rapid-responsive motions with the CLCP composite materials are successfully induced by photoirradiation, which leads to novel three-dimensional movements such as an inchworm walk and a flexible robotic arm motion. These results show the high possibility of numerous applications based on CLCP composites that can convert light energy directly into mechanical work and move without any batteries or electric wires.

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