Photo-activated bimorph composites of Kapton and liquid-crystalline polymer towards biomimetic circadian rhythms of *Albizia julibrissin* leaves†

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Circadian rhythm is a built-in bioclock widely existing in living organisms, not only in animals but also in plants. Particularly, circadian rhythm is of great importance for the growth of plants. To mimic the circadian rhythm behavior of *Albizia julibrissin* leaves, we designed photo-activated bimorph composites with several kinds of photoresponsive liquid-crystalline polymers and commercially-available polyimide (Kapton). Compared with conventional photo-actuators, the fabricated bimorph composite possesses good mechanical properties, a large displacement angle and a fast photoresponsive rate at room temperature. Upon irradiation with actinic light, unique photomechanical behaviors were observed, in which the bimorph composites always bent towards the Kapton layer side independent of the incident direction of UV light, as a result of the photoinduced volume expansion of the liquid-crystalline polymer layer. To further explore the photomechanical properties, the $F$ (photoinduced driving force)–$I$ (light intensity) and $\theta$ (displacement angle)–$I$ (light intensity) relationships of the photo-activated bimorph composites were theoretically proposed based on a classical double beam model. Taking advantage of their sensitivity to light intensities, artificial *Albizia julibrissin* leaves exhibiting circadian rhythms upon UV irradiation with time varying light intensities (simulating the sunlight change from sunrise to sunset) were successfully fabricated, which may extend the versatility of biomimetic research studies.

Introduction

Over millions of years of evolution, plants have adapted to the natural world in a perfect manner. Several movements of plants have been simulated by soft actuators, including the stimuli-responsive motion of *Mimosa pudica*, the gripping of flytraps, the burst of seedpods, and the winding of cucumber tendrils. One typical example of plant movement is the “sleeping” behavior (circadian rhythm) of *Albizia julibrissin* (known as silk tree in China) leaves. This “sleeping” movement is of pivotal importance to the growth of plants, which helps them to prevent water evaporation and keep warm at night. Although the molecular mechanism of controlling the circadian rhythm has been discovered by the 2017 Nobel Prize laureates, biomimetic research on plant circadian rhythm has not been reported yet. The opening and closing movements of symmetric leaflets are thought to be strongly related to the inherent structure of the leaves and environmental stimuli (in this case, sunlight). As shown in Fig. 1a, a wide variety of photoreceptors, such as phytochromes (for IR in sunlight) and cryptochromes (for UV and blue light), are located in the palisade tissue to “sense” sunlight. In addition, the structure of the pinnate leaflets is crucial for such “sleeping” behavior. The cells at the stipule of each leaflet act as the movement executors, propelling the leaflets to open or close by turgor pressure changes based on the illumination information offered by the photoreceptors. To mimic these sunlight-stimulated movements, it is necessary to introduce stimuli-responsive functional materials into the elegantly designed structures. Several works have reported bilayer-structured actuators composed of liquid crystalline elastomer layers and stimuli-responsive layers, e.g. thermal responsive or humidity-responsive materials.

Due to the excellent photoresponsive characteristics, azobenzene-containing liquid-crystalline polymer (LCP) is one of the most fascinating choices as the photoreceptor. Upon irradiation with actinic light, the molecular shape change of rod-like azobenzenes...
upon trans–cis photoisomerization can be autonomously amplified into visible macroscopic motion in LCP films by the synergistic effect, ensuring that the polymer system is suitable for light-driven actuators.\textsuperscript{15–18} Thus, a series of macroscopic motions have been observed such as oscillation,\textsuperscript{18,19} wave propagation,\textsuperscript{20–22} self-origami,\textsuperscript{23} controlled microfluidics,\textsuperscript{24} helical movement,\textsuperscript{25–28} motor, rotational,\textsuperscript{29,30} and so on.\textsuperscript{21,31} Moreover, LCPs could also provide robust mechanical properties and resistance to hostile environments after a chemical crosslinking treatment. These unique features enable light-responsive LCPs to be desirable for simulation of the circadian rhythms of silk tree leaves. To the best of our knowledge, there are no reports about such biomimetic work so far.

In this paper, we designed biomimetic leaves with photo-activated bimorph composites (Fig. 1b), which could accurately reproduce the innate structure and the circadian rhythm function of silk tree leaves. Specifically, the artificial leaves were crafted with a bilayer composite film composed of commercial polyimide (Kapton) substrate and one layer of photoresponsive LCP by a facile drop casting method. The LCP layer acts as both the photoreceptor and the movement executor. The bimorph composite film displayed a dramatic photomechanical bending towards the Kapton layer due to the photoinduced volume expansion of the photoresponsive LCP layer. In addition, photomechanical behavior of the bimorph composite films with varied thickness was systematically studied, and the relationship between the displacement angle ($\theta$) and the light intensity ($I$) of the photo-activated bimorph was quantitatively analyzed for the first time. As $\theta$ is sensitive to UV intensity change, smart artificial leaves displayed gradual opening and closing as the UV intensity switched. This work may expand the diversity of artificial autonomous movement systems and provide theoretical insights into photomechanical properties of photo-activated bimorph composites.

### Results and discussion

#### Design of the biomimetic system

As shown in Fig. 1a, the circadian rhythm behaviour of natural silk tree leaves is usually accomplished \textit{via} the synergy effect between the photosensitization process and the movement controlling process.\textsuperscript{9} The former process is achieved through the photoreceptors distributed in the palisade tissue under the blade surface of the leaflet (Fig. 1a, right panel). While the latter process relies on the turgor pressure change of cells induced by sunlight. Accordingly, we designed a bilayer structure with a Kapton bottom surface and LCP top surface of the artificial leaves, as shown in Fig. 1b. The photoresponsive LCP layer was designed as the outer surface of the artificial leaves, working as the photoreceptor and the movement executor, while the Kapton layer was a photo-inert layer. Furthermore, the outer surface was chemically crosslinked to enable the artificial leaves to accommodate harsh weather and environments.

#### Design of molecular structure and bimorph preparation

Fig. 2a shows the molecular structure of random LC copolymers P(M\textsubscript{6}ABOC\textsubscript{2}-r-M\textsubscript{6}AzPy) obtained by copolymerization of two monomers, M\textsubscript{6}ABOC\textsubscript{2} and M\textsubscript{6}AzPy. The homopolymer PM\textsubscript{6}ABOC\textsubscript{2} exhibiting a typical nematic phase has been widely applied in the design of photoresponsive LCP,\textsuperscript{32,33} endowing the copolymer with LC ordering. The introduction of the M\textsubscript{6}AzPy monomer containing one active pyridine group provides the possible crosslinking site. Two random copolymers P82 (80 mol\% of M\textsubscript{6}ABOC\textsubscript{2} and 20 mol\% of M\textsubscript{6}AzPy) and P55 (50 mol\% of M\textsubscript{6}ABOC\textsubscript{2} and 50 mol\% of M\textsubscript{6}AzPy) were synthesized, respectively. Their molecular weights and thermal properties are listed in Table 1.
Both P55 and P82 displayed a typical Schlieren texture of nematic phase under observation of a polarizing optical microscope (POM, Fig. S1, ESI†). The homopolymer PM6ABOC2 had the broadest LC temperature range of about 54 °C. As the molar ratio of M6AzPy increased to 50%, the LC range of the copolymer reduced to only 4 °C, accordingly. To keep the liquid crystalline properties, the ratio of M6AzPy should be kept no more than 50%.

As shown in Fig. 2b, the bilayer film was fabricated by a facile drop-casting method following our previously-reported strategy.34,35 The LCP solution was first drop casted onto the Kapton film. After solvent evaporation, the composite film was annealed at the LC temperature (P55 at 105 °C and P82 at 130 °C) and slowly cooled to room temperature to allow the mesogens to distribute in a nematic manner. Finally, the annealed film was crosslinked by vapor–solid intermolecular quaternization in a sealed container at 60 °C. It is worth noting that thickness of the LCP layer could be tuned by altering the concentration of the polymer solution. The thickness of the Kapton layer was fixed at 12.5 μm, as indicated in Fig. S2 (ESI†). The corresponding LCP layer thickness, the whole bilayer film thickness and the ratio of the LCP layer prepared from the LCP solutions with concentrations ranging from 4 mg mL⁻¹ to 12 mg mL⁻¹ are summarized in Fig. S3 (ESI†).

### Photoreactive behaviour of the crosslinking system

Successful crosslinking of random copolymers can be proved by the appearance of colour changes, and FTIR and UV-vis absorption spectroscopy. Digital images of a series of composite films during the preparation process are shown in Fig. S4 (ESI†). The colour change of yellow-to-brownish occurred as the quaternization reaction.40,41 In addition, as shown in Fig. 3b, the new peak at 1634 cm⁻¹ in the FTIR spectra is characteristic of the positively charged pyridine group, indicating the occurrence of the quaternization reaction.37–39

![Fig. 3](image-url) (a) UV-vis absorption spectra of PM6AzPy homopolymer as the crosslinking time increases. (b) FTIR spectra of P55 before and after chemical crosslinking.

Herein, the chemical crosslinking has two functions: (1) enhancement of the solvent resistance. The random copolymer before treatment can be easily dissolved in DMF, THF or chloroform, forming clear transparent solutions. While the crosslinked LCP film is intact in organic solvents without dissolution or peeling off from the Kapton layer (Fig. S5, ESI†). (2) Acceleration of the photosensitive rate by changing the azopyridine group into the famous type of push–pull azobenzene. Then the photo-responsive behaviours of the crosslinked and un-crosslinked polymer films were studied upon irradiation with 365 nm UV light (100 mW cm⁻²).

As shown in Fig. 4b, the absorption of the quaternized P55 film can be regarded as the superimposition of two types of azobenzene chromophores: ethoxy azobenzene (ABOC2) and quaternized azopyridine (AzPy). As the polymer reaches a photostationary state, the peak at 311 nm is consistent with the responsive feature of the ABOC2 part,42 while the peak at 403 nm is attributed to quaternized AzPy groups. The former didn’t participate in the quaternization reaction, retaining the original responsive features of PM6ABOC2 shown in Fig. S6a (ESI†) (the π–π* transition absorption peak decreased and shifted to lower wavelength). The quaternization reaction converted azopyridine into a pseudo-stilbene type of electron-push–pull azobenzene, which thus had a great impact on the photoreactive behaviour. Extremely fast cis-to-trans thermal isomerization (in several ms) occurs in quaternized PM6AzPy according to former reports.39,43 As light was turned off, cis-molecules instantly recovered to the initial trans state, before the spectrometer could detect it, thus leading to stable UV-vis absorption spectra in Fig. S6c (ESI†).

In terms of response rate, pure PM6ABOC2 film reached its photostationary state within 5 min of photoirradiation.

![Fig. 4](image-url) UV-vis absorption spectra of the P55 film before (a) and after (b) the chemical crosslinking. The films were exposed to UV light at 365 nm (100 mW cm⁻²).
ESI exposure time did not increase the displacement angle (Fig. S7, reached the maximum bending angle, further elongation of connecting two ends of the film, inserted in Fig. 5a) within 2 s angle (defined as the angle between normal line and the line response rate, the film reached its maximum displacement almost no obvious difference in the response rate once the discussed above, it is expected that the addition of azopyridine polymers follow a sequence of: crosslinked PM6AzPy > PM6AzPy > crosslinked P55 > P55 > PM6ABOC2. The photoresponsive behaviour of P82 was almost the same as that of P55, which was employed in the following work for its better optical transparency.

**Photomechanical behaviours of the bimorph composites**

As the photoresponsive features have been clarified above, we now turn to the photomechanical behaviour of the bimorph composite. Upon irradiation with UV light, they exhibited rapid and substantial photoinduced bending motion towards Kapton side. Fig. 5a and b show representative snapshots of the bimorph composite film under photoradiation and recovery processes after removal of light (Movie S1, ESI†). With a rapid response rate, the film reached its maximum displacement angle (defined as the angle between normal line and the line connecting two ends of the film, inserted in Fig. 5a) within 2 s and recovered back within 1.5 s under room light. After the film reached the maximum bending angle, further elongation of exposure time did not increase the displacement angle (Fig. S7, ESI†). Based on the response rate difference between PM6ABOC2, PM6AzPy, P55, crosslinked P55 and crosslinked PM6AzPy we have discussed above, it is expected that the addition of azopyridine group and crosslinking would enhance the photoresponsive rate of the bimorph composite. However, we found that there was almost no obvious difference in the response rate once the bimorph composites with different kinds of LCPs were prepared. As indicated in Fig. S8 (ESI†), all the bimorph composite films demonstrate a response time between 1.3 s to 2.0 s and a reverse time of 1.5–2.8 s. It could be concluded from the results that the UV-response rate of the bimorph composite film was not mainly determined by the response rate of the photoactive layer of LCPs.

Now we turn to the bending direction of the bimorph composite, as UV light shined on the bimorph, the film always bent towards the Kapton side independent of the incident direction, as shown in Fig. 5a and b (the inserted schemes). As UV light irradiated from either side of the bilayer film, both displacement angle and driving force were almost equal within the margin of error (Table S1, ESI†). This unique photomechanical behavior of the bimorph composite film is different from that of the mono-domain oriented LC elastomers or homogeneous LC/polymer composite films,2,15,44–48 which often bend towards the light source due to the anisotropic volume contraction along the long axis of mesogens. In our strategy, the bimorph composite film containing crosslinked LCP demonstrates a large displacement angle even though the mesogens were randomly distributed. Barrett et al. proved the light-induced expansion effect of azobenzene-containing polymers via ellipsometry and neutron reflectometry.49–51 As our group has recently reported, one crosslinked LCP system with azobenzene groups located in the side chain instead of the crosslinker expanded upon UV irradiation as free volume is needed for the photochemical process of trans–cis isomerization.51,52 Taking account of the photoinduced expansion theories and similar response rates of the bimorph composites with different types of LCPs, we propose that the photo-actuation behavior should be rationalized as follows: UV irradiation triggered volume expansion of the photoactive LCP layer and induced stress within a short period between the two layers, thus the stress pushes the bimorph composite film to bend towards the photo-inert Kapton side (Fig. 5c). That is, the photomechanical behavior of the bimorph composite should originate from the bilayer structure instead of the type of photoresponsive LCPs.

**Theoretical model for photomechanics of the bimorph composites**

Since the bilayer structure of the composite film has a major effect on its photomechanical properties, we then systematically investigated the influence of the LCP layer thickness and light intensity of UV light. Fig. 6a and b illustrate the photoinduced driving force with varied LCP layer thickness at different light intensities. UV illumination (100 mW cm⁻²) triggered an immediate increase of the driving force to −72 mN (the negative value means the strip was bent rather than straightened). All the samples displayed very good reversibility without detectable attenuation as the cycle time increased.

As shown in Fig. 6a, a thicker LCP layer and a stronger light intensity could produce a larger driving force. Ideally, the photoinduced driving force should be proportional to the thickness of the LCP layer when the Kapton layer thickness was fixed. Consequently, we established the F–I relationship according to the classical double-layer beam theory. An assumption

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**Fig. 5** Photomechanical behaviours of the LCP–Kapton bimorph composite films: (a) Snapshots of a composite film during the UV exposure process, UV light was shined on the LCP side from the left. From left to right: before UV, UV on for 2 s, recovery for 1.5 s. (b) UV light shined on the Kapton side from the left. Inset is a scheme for the bending behaviour of bilayer film (green: LCP layer; yellow: Kapton layer). (c) Scheme illustrating photoisomerization induced expansion of the LCP layer.
should be made that the cross-sections of the strip originally plane and perpendicular to the axis remain plane during the photomechanical bending and become perpendicular to the curved axis of strip. The volume expansion induced strain of the LCP layer could be calculated as follows:

\[ e_{\text{drive}} = F / E_1 h_1 b = 2I \] (1)

\[ F = 2E_1 h_1 bI \] (2)

\( E_1 \) Young’s modulus of the LCP layer; \( h_1 \) thickness of the LCP layer; \( b \) width of the bilayer strip; \( F \) driving force; and \( I \) UV light intensity.

\( E_1 \) was measured by AFM in contact mode as 533 MPa (the force curve is given in Fig. S8, ESI†). \( x \) is a constant that could be determined from the measured data. To ensure the accuracy of the constant, a thin LCP film with a thickness of 2.5 \( \mu m \) under UV irradiation was chosen to obtain \( x = 0.0094 \). Accordingly, the scale factors for samples with thicknesses of 4.7 \( \mu m \), 7.2 \( \mu m \) and 9.5 \( \mu m \) were \( k_{4.7} = 0.706, k_{7.2} = 1.082, \) and \( k_{9.5} = 1.353 \), respectively. The calculated relationship for LCP samples with varied thicknesses are shown as solid lines. For all samples, the driving force is in proportion to the UV light intensity. As the LCP film thickens, the scale factor \( k \) also increases. That is, a larger driving force can be produced in a thicker film upon irradiation using the same UV light. For comparison, the experimental data were depicted as a scattergraph in Fig. 6c. Since \( x \) was obtained from a thin sample (a thickness of 2.5 \( \mu m \)), the scattergraph and the calculated solid line were exactly consistent with each other (the green line). While for thicker films, the measured driving force deviated a little from the calculated data. The thicker the film, the larger the deviation. This phenomenon could be rationalized as follows: as the LCP layer becomes thicker, the transparency of the film decreases owing to the scattering effect of randomly-distributed mesogens. Thus, the incident light dissipates within the LCP layer, leading to a driving force that was slightly smaller than the theoretical values.

Fig. 6d shows variation of the displacement angle \( \theta \) with the light intensity. Obviously, the thicker film displayed a larger displacement angle at the fixed incident light, which corresponds well to the change of driving force in Fig. 6c. The displacement angle \( \theta \) can be fitted according to eqn (3):

\[ \theta = \frac{-3E_1E_2h_1h_2(h_1 + h_2)L}{3(E_1h_1^2 - E_2h_2^2)^2 - 4(E_1h_1^3 + E_2h_2^3)((E_1h_1 + E_2h_2)^2)} \times I \] (3)

Here, \( E_2 \) and \( h_2 \) represent the Young’s modulus and thickness of the Kapton film, respectively. \( L \) is the length of the bilayer strip. On account of eqn (3), the displacement angle \( \theta \) should be proportional to light intensity (\( I \)). In addition, the slope is related to the thickness of the LCP layer \( h_1 \), as \( L, x, E_2 \) and \( h_2 \) are all constants. Based on the calculation, as \( h_1 \) increases, the slope will also elevate accordingly. This theoretical analysis fits well with the results shown in Fig. 6d.

**Biomimetic “sleeping” behaviours of silk tree leaves**

The unique photomechanical bending behaviour of the bimorph makes them a perfect choice for mimicking the “sleeping” behaviour of silk tree leaves. Thus, we designed artificial leaves with two pieces of the bimorph composite strips fixed face-to-face (LCP layer-to-LCP layer), and one end of the twin strips was fixed on a foldback clip. As light was incident, the photoreceptors of the LCP layer absorbed the light energy, and photoinduced expansion occurred, propelling the twin “leaflets” to open. In nature, silk tree leaves start to unfold at dawn, when the sunlight is still dim. Then, the leaves gradually open to its maximum angle as the sun rises above the horizon. Finally, as the sun goes down at dusk, the opened leaves gradually return to the closed state for “sleeping”. To simulate the cycle of sunlight change, we applied UV light with a gradient light intensity (from 20 mW cm\(^{-2}\) to 100 mW cm\(^{-2}\), 5 s for each stage), as shown in Fig. 6a, b and Movie S2 (ESI†).

Just as expected, the structure of symmetrically-distributed pinnately compound leaves is critical for their “sleeping” behaviours. Although the effective area exposed to sunlight is smaller in pinnately compound leaves compared with that of a single whole leaf, most of the “sleeping” plants, such as peanuts, Oxalidaceae and *Mimosa pudica*, have pinnately compound leaves instead of a whole single leaf. To this end, we’ve also designed artificial “leaflets” along the “rachis”. This design was achieved by cutting a bilayer film as illustrated in Fig. 7c. To obtain sufficient light, displacements of leaflets on the two sides along the rachis were allowed. We demonstrated the opening and closing movements of artificial compound leaves with four pairs of leaflets, as marked on the top view in Fig. 7d and Movie S3 (ESI†). Side views of the movements are also given in Fig. 7e.
Further purification. The monomer 6-(4-((4-ethoxyphenyl)diazenyl)phenoxy)hexyl methacrylate (M₆ABOC₂) and 6-(4-(pyridylazo)phenoxy)hexyl methacrylate (M₆AzPy) were synthesized according to the literature report. 32, 33, 54-56 M₆ABOC₂: 1H NMR (δ, CDCl₃): 7.81 (m, 4H), 6.90 (m, 4H), 6.03 (s, 1H), 5.43 (s, 1H), 4.10 (t, 2H), 4.04 (m, 2H), 3.95 (t, 2H), 1.87 (t, 6H), 1.79-1.74 (m, 2H), 1.69-1.63 (m, 2H), 1.37-1.49 (m, 4H). M₆AzPy 1H NMR (δ, CDCl₃): 8.79 (d, 2H), 7.96 (d, 2H), 7.69 (d, 2H), 7.03 (d, 2H), 6.12 (s, 1H), 5.56 (s, 1H), 4.19 (t, 2H), 4.08 (t, 2H), 1.96 (s, 3H), 1.80-1.90 (m, 2H), 1.65-1.80 (m, 2H), 1.43-1.65 (m, 4H).

Synthesis of the random copolymers

The random copolymers were synthesized by free radical polymerization of the two monomers with different feed ratios. To obtain the random copolymer (P55 as an example), M₆ABOC₂ (410 mg, 1.0 mmol), M₆AzPy (368 mg, 1.0 mmol), azodiisobutyronitrile (AIBN, 4.2 mg, 0.025 mmol) and anhydrous dimethylformamide (DMF, 2.0 mL) were added into a flask. After freezing and drawing 3 times, the reaction was proceeded at 70 °C with stirring for 48 h. After reaction, the product was precipitated in methanol 3 times, and dried in a vacuum oven for 24 h. Yield: 51.4%. P55: 1H NMR (δ, CDCl₃): 8.63 (s, 2H), 7.77-7.71 (m, 6H), 7.54 (s, 2H), 6.81 (m, 6H), 3.92-3.83 (m, 10H), 1.66 (m, 4H), 1.54 (m, 4H), 1.43-1.24 (m, 12H) 0.83-0.98 (m, 9H).

Preparation of the bimorph composite film

Commercially-available Kapton film (thickness: 12.5 μm) was rinsed in ethanol and deionized water successively. 12.0 mg of the random copolymer P55 was dissolved in a mixed solvent (DMF/THF = 1:9) and passed through a tetra-fluoroethylene filter to remove insoluble impurities. After that, the filtered solution was drop casted onto Kapton film with the size of 2.5 cm × 7.5 cm. After evaporation of the solvent at room temperature (25 °C) for 24 hours, the composite film was annealed at the LC temperature (105 °C for P55; 130 °C for P82) in a vacuum oven for 12 hours so that the mesogens homedistributed randomly on the Kapton substrate. At the same time, the residual solvent can be removed during the annealing process. The film thickness of the LCP layer can be tuned by altering the concentration of the polymer solution.

Crosslinking of LCP by quaternization reaction

Quaternization reaction was carried out within sealed petri dishes. A sponge with DIB crosslinker was placed at the bottom of the container, and the bimorph composite film was made to stick on top of the container, the reaction was conducted at 70 °C for 6 hours. Finally, the crosslinked film was cut into strips of 3 mm × 20 mm for further study.

Characterizations

FTIR measurement was conducted on a FTIR spectrometer (spectrum II, Perkin Elmer) in transmission mode. UV-vis absorption spectrum was recorded on a Lambda 750 UV/vis/NIR spectrophotometer (Perkin Elmer). AFM force curve was obtained by MultiMode 8 (Bruker) with contact mode in air. The Young’s modulus was obtained by the average of 5 points.
on the same sample. Thermal property of the random copolymers was measured via DSC 8000 (Perkin Elmer). Molecular weight of the copolymer was obtained via GPC (Waters 1515). Driving force of the bilayer film was tested using a tensile test machine (Jinan LianGong). Polarizing optical microscopic (POM) images were observed via Zeiss AXIO scope optical microscope equipped with a hot stage. The thickness of the bilayer film was measured using a scanning electron microscope (SEM, S-4800, HITACHI) at an accelerating voltage of 2.0 kV. The thickness of the bilayer film was measured via a micrometer.

Conflicts of interest

There are no conflicts to declare.

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Notes and references