Supporting Information for

Photo-activated Bimorph Composites of Kapton and Liquid-Crystalline Polymer Towards Biomimetic Circadian Rhythms of Albizia Julibrissin Leaves

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1. Thermal properties of the LCPs

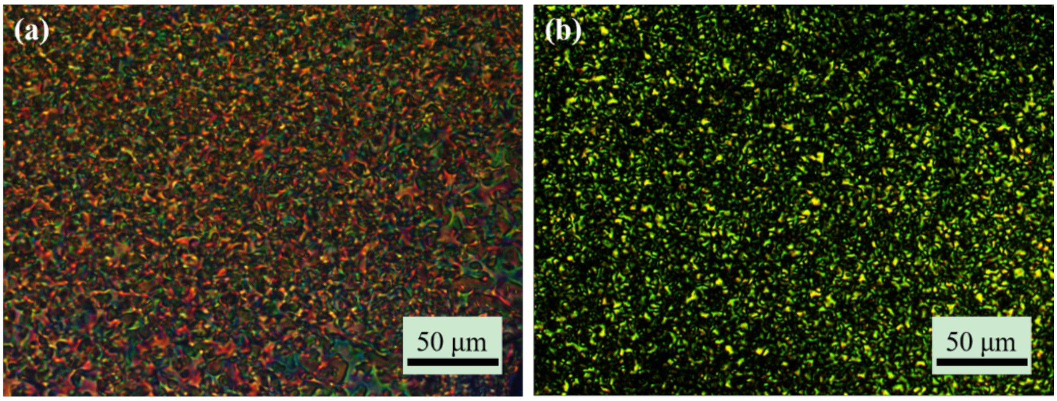


Figure S1. Liquid crystalline texture of (a) P55 at 105 °C and (b) P82 at 130 °C.

2. Thickness control of the LCP layer

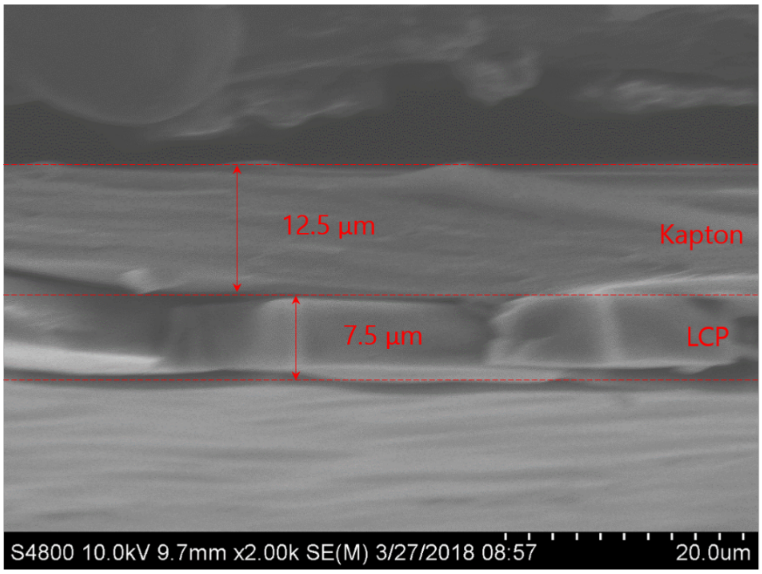


Figure S2. SEM image of a typical bilayer film cross-sectional view. The upper layer is LCN layer (Crosslinked P55), the thickness h_1=7.5 µm; the lower layer is kapton layer, the thickness h_2= 12.5 µm. Concentration: 9 mg/mL (DMF/THF=9:1); Solution dose: 1 ml; size of the substrate: 2.5 cm×7.5 cm.

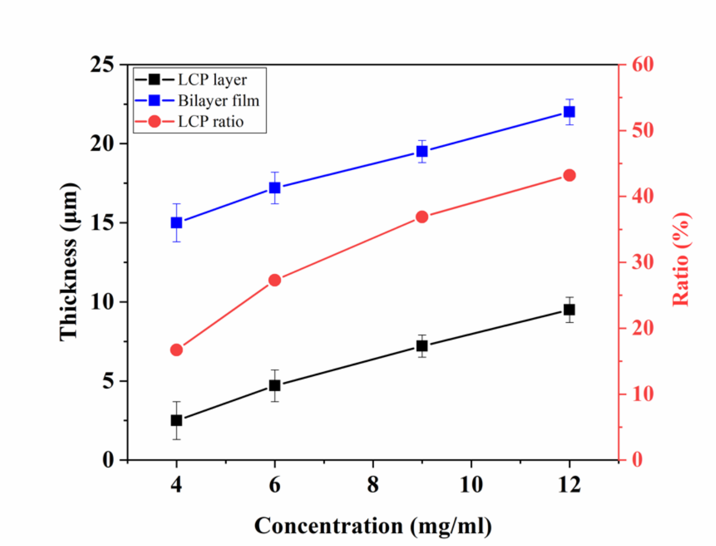


Figure S3. Controlling bilayer film thickness via tuning concentration of LCP solutions. Black curve: average thickness of LCP layer prepared from varied concentration. Blue curve: corresponding thickness of the bilayer film. Red curve: the ratio of LCP layer thickness to bilayer film thickness. As the concentration increased from 4 mg/mL to 12 mg/mL, LCP layer was thickened from 2.5 µm to 9.5 µm.

3. Crosslinked LCP bilayer film

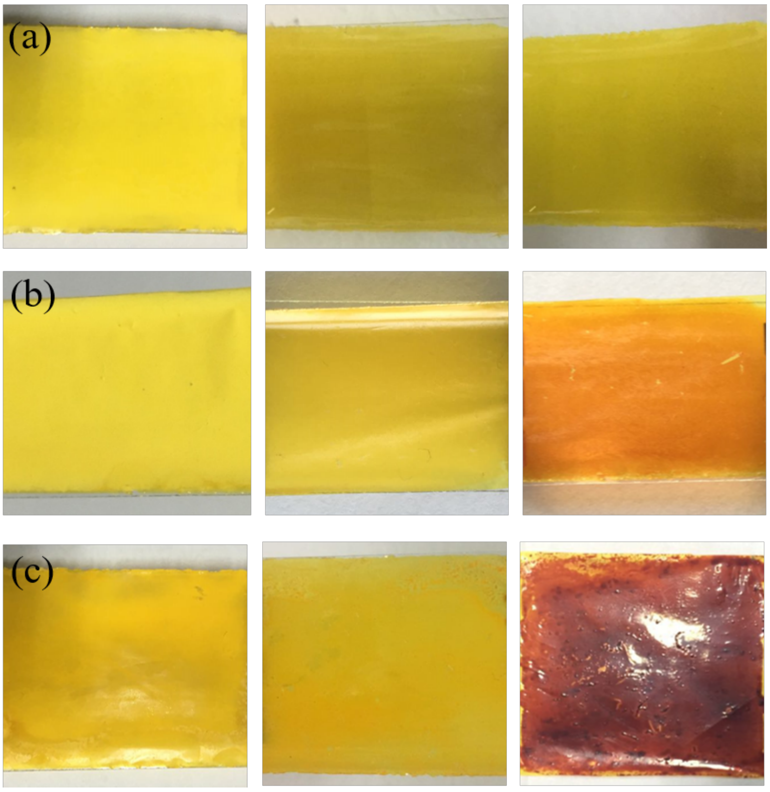


Figure S4. Images of the bilayer film, as-prepared (left column), after thermal annealing (middle column) and after crosslinking (right column). (a) PM_6ABOC_2 homopolymer; (b) P82 random copolymer; (c) P55 random copolymer.

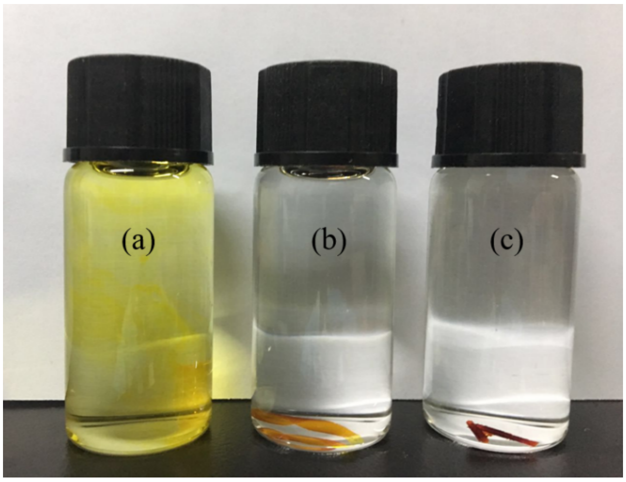


Figure S5. The bilayer film in dimethylformamide (DMF) solution. (a) Uncrosslinked P55; (b) Crosslinked P82; (c) Crosslinked P55.

4. Photoresponse of the uncrosslinked polymers

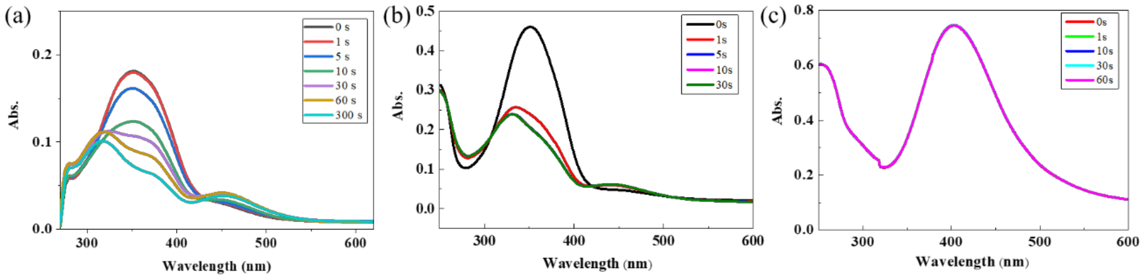


Figure S6. (a) UV-responsiveness of PM6ABOC2 homopolymer. (b) UV-response of PM6AzPy homopolymer before crosslinking. (c) UV-response of uncrosslinked P55.

5. Displacement and driving force change over time of the bimorph composite film

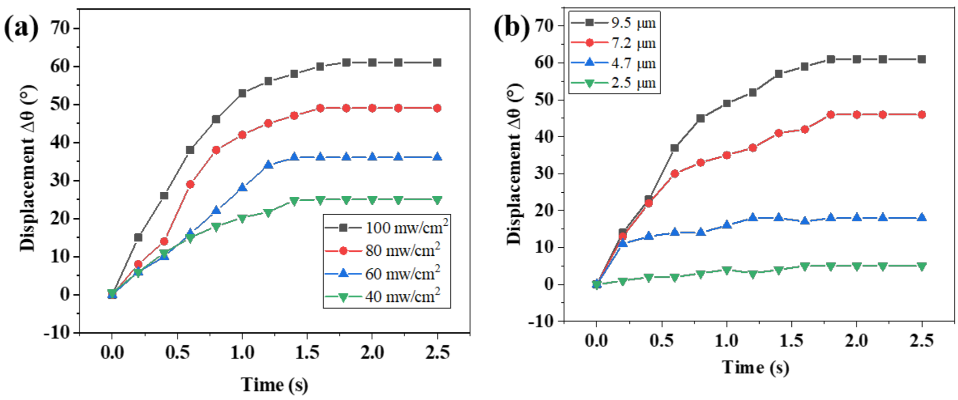


Figure S7. (a) Bending displacement change over time at varied light intensities. (Size: 20 mm×3 mm ×22 μm). (b) Bending displacement change with varied thickness. (Light intensity: 100 mW/cm^2)

Table S1 Driving force and displacement angle of bilayer film

	Driving force F (mN)		Displacement angle θ (°)	
	LCP side	Kapton side	LCP side	Kapton side
9.5 μm	157.4±4	161.8±3	65.2±2	64.8±3
7.2 μm	110.7±6	116.1±6	51.7±3	52.1±3
4.7 μm	69.7±3	66.3±5	30.8±2	30.4±2

Note: the UV intensity were kept at 100 mw/cm^2 in above experiments.

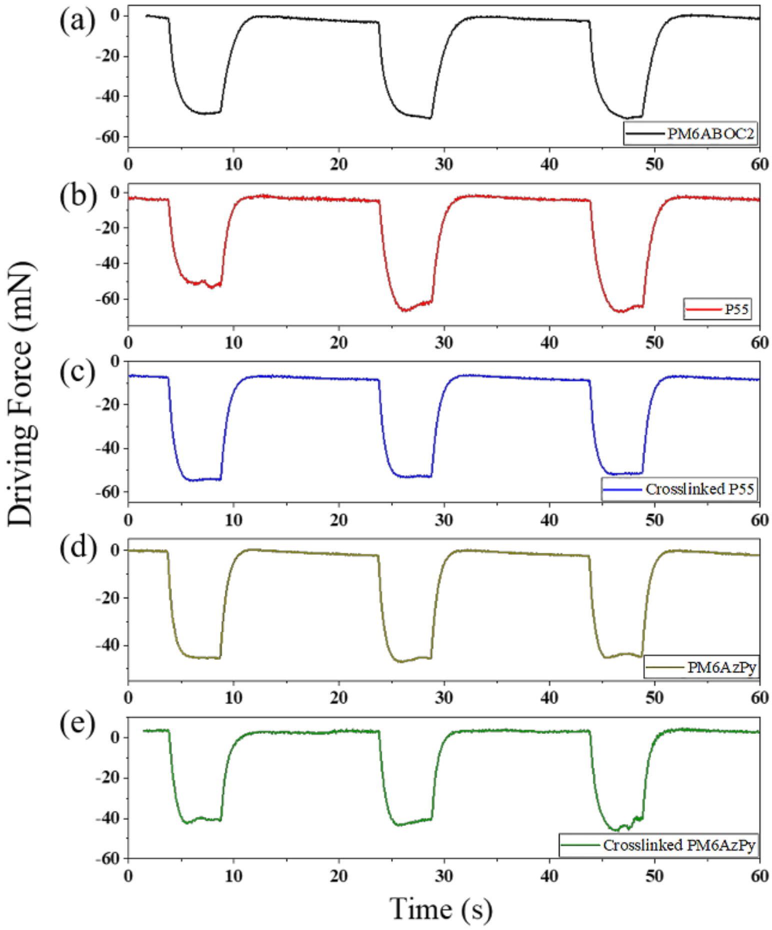


Figure S8. Change of driving force upon UV irradaition (100 mw/cm^2) of the bimorph composited with different types of azobenzene-containing polymers. (a) PM6ABOC2; (b) P55; (c) Crosslinked P55; (d) PM6AzPy; (e) Crosslinked PM6AzPy.

6. Youngs'modulus of the LCP layer

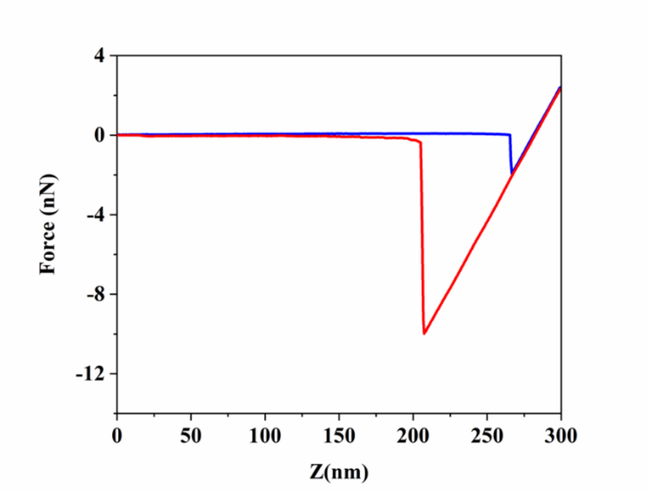


Figure S9. A typical AFM Force curve of quaternized P55.

7. Supplementary note: derivation of equation (3) in the main text

E_1 Elastic modulus of the LCP layer

h_1 Thickness of the LCP layer

E_2 Elastic modulus of substrate

h_2 Thickness of substrate

F Driving force

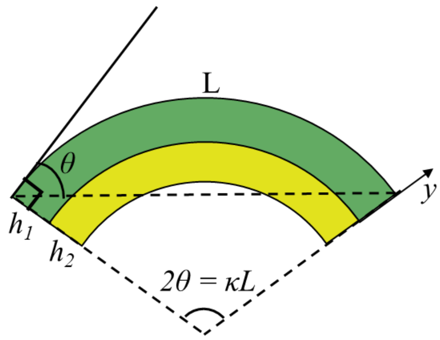
b Width of the film

L Length of the film

θ Bending angle of the film

κ Bending curvature

I Light intensity of UV light



A neutral layer is assumed at y=0, where the strain is set as ε_b.

By geology relationship, the angle between two tangential line of the curved film is twice that of the measured angle θ.

Assuming that the crosslinked LCP layer is free at both ends without substrates, the expansion induced stain of LCP layer is calculated as the following,[1]

$$\varepsilon_{drive} = \frac{F}{E_1 b h_1} = \alpha I \qquad (1)$$

The elastic strain of LCP layer at curved state should be,

$$\varepsilon_1 = \varepsilon_b - \varepsilon_{drive} + \kappa y \qquad (2)$$

κ is the curvature, which is reciprocal of the radius;

y is the coordination value in thickness direction.

The elastic stain substrate layer is,

$$\varepsilon = \varepsilon_b + \kappa y \qquad (3)$$

When the system reaches equilibrium, that is, the film reaches its maximum bending angle.

The overall equilibrium equation is,

$$\int_{-h_2}^{0} E_2 \varepsilon_2 \, dy + \int_{0}^{h_1} E_1 \varepsilon_1 \, dy = 0 \qquad (4) \qquad \text{Force Equilibrium}$$

$$\int_{-h_2}^{0} E_2 \varepsilon_2 \, y dy + \int_{0}^{h_1} E_1 \varepsilon_1 \, y dy = 0 \qquad (5) \qquad \text{Moment Equilibrium}$$

With equation (4) and (5), curvature κ is solved as,

$$\kappa = \frac{-6E_1E_2h_1h_2\,(h_1+h_2)}{3\,(E_1{h_1}^2 - E_2{h_2}^2)^2 - 4(E_1{h_1}^3 + E_2{h_2}^3)(E_1h_1 + E_2h_2)} \alpha I \qquad (6)$$

Thus the bending angle is,

$$\theta = \frac{\kappa L}{2} = \frac{-3E_1E_2h_1h_2\,(h_1+h_2)\,L}{3(E_1{h_1}^2 - E_2{h_2}^2)^2 - 4\,(E_1{h_1}^3 + E_2{h_2}^3)(E_1h_1 + E_2h_2)} \alpha I \qquad (7)$$

8. Supplementary Movie:

Movie 1: The bending behavior of bimorph composite film as UV irradiated from both sides. UV light is incident from left side.

Movie 2: Opening and closing movement of artifacial leaves with UV irradiation simulating the sunlight change. UV light was shined from left side in the movie.

Movie 3: Opening and closing movement of artificial pinnate compound leaves upon UV on and off.

References

(1) Q. Ge, C. K. Dunn, H. J. Qi, M. L. Dunn, Active origami by 4D printing. *Smart Mater. Struct.* 2014**, 23**, 094007.