Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Light-Driven Autonomous Self-Oscillation of Liquid-Crystalline Polymer Bimorph Actuator

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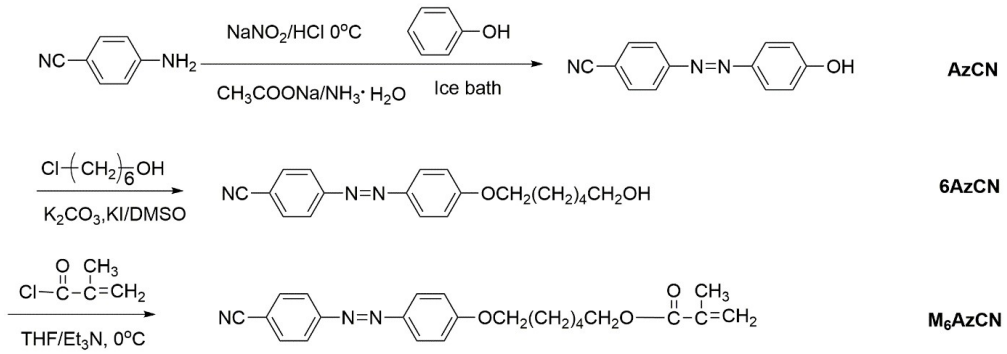


Scheme S1. Synthesis of the azobenzene-containing monomer M_6AzCN.

The monomer M_6AzCN was synthesized by the diazo-coupling reaction between 4-cyanoaniline and phenol in the presence of sodium nitrite and hydrochloric acid and the following reaction with 6-chloro-1-hexanol and methacryloyl chloride.[S1] The ^{1}H NMR spectrum of M_6AzCN was recorded in $CDCl_3$ solution, as shown in Scheme S1. ^{1}H NMR (500MHz, $CDCl_3$, 25 ˚C, TMS): δ 7.94-7.93 (4H, d), δ 7.78-7.80 (2H, d), δ 7.0-7.02 (2H, d), δ 6.10 (1H, s), δ 5.55 (1H, s), δ 4.15-4.18 (2H, t) δ 4.05-4.08 (2H, t), δ 1.94 (3H, s), δ 1.85 (2H, m), δ 1.76 (2H, m), δ 1.4-1.6 (4H, m).

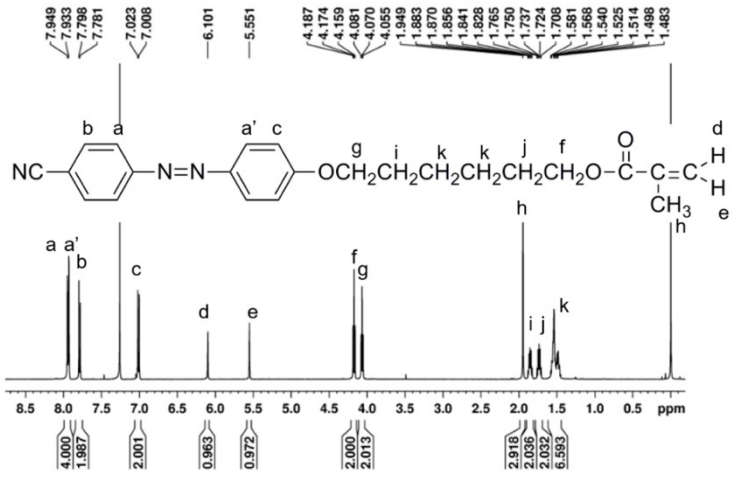
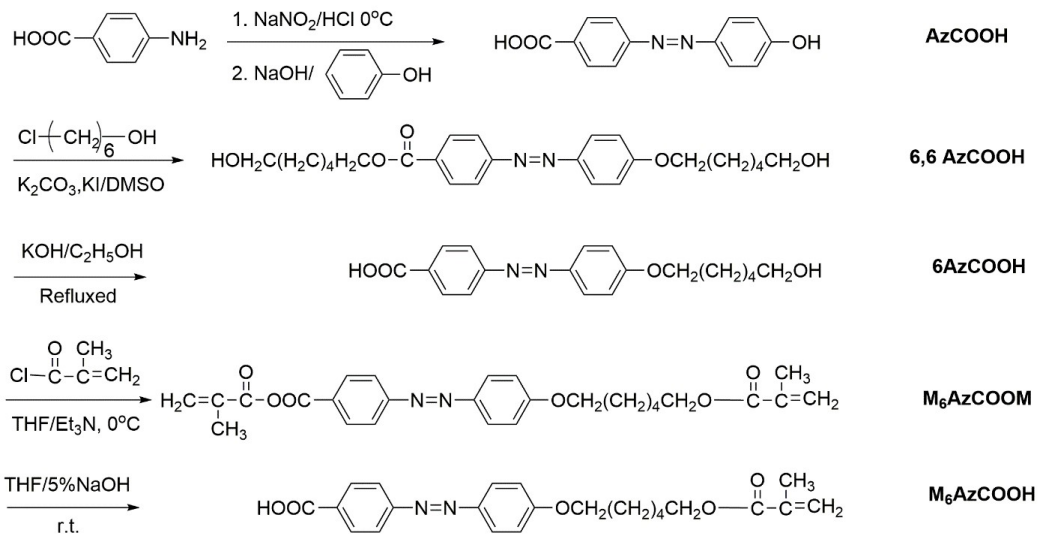


Fig. S1. ^{1}H NMR spectrum of the monomer M_6AzCN



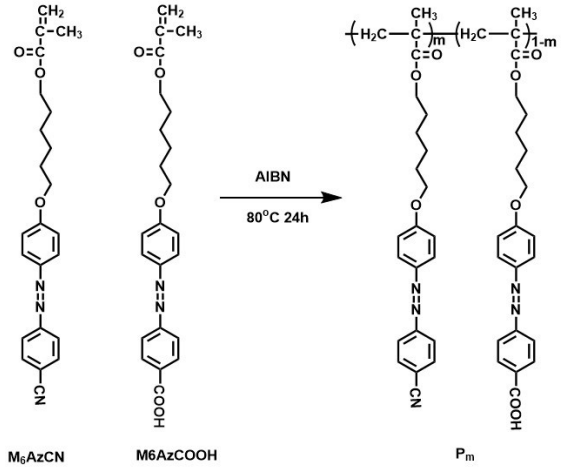
Scheme S2. Synthesis of the monomer M_6AzCOOH.

The monomer 6-(4-((4-Carboxylphenyl)diazenyl)-phenoxy) hexyl methacrylate (M_6AzCOOH) was synthesized according to the literature reported.[S2] The ^{1}H NMR spectrum of M_6AzCOOH was recorded in DMSO-d_6 solution, as shown in Fig. S2. ^{1}H NMR (500MHz, DMSO-d_6, 25 ˚C, TMS): δ 13.16 (1H, m), δ 8.11-8.13 (2H, d), δ 7.92-7.93 (4H, d), δ 7.13-7.15 (2H, d), δ 6.0 (1H, s), δ 5.66 (1H, s), δ 4.09-4.12 (4H, t), δ 1.87 (3H, s), δ 1.77 (2H, m), δ 1.65 (2H, m), δ 1.35-1.5 (4H, m).

Fig. S2. ^{1}H NMR spectrum of the monomer M_6AzCOOH.

Copolymer $P_{0.9}$. The monomers M_6AzCN (400mg, 1mmol) and M_6AzCOOH (100 mg, 0.26 mmol) and AIBN (1wt%, 5 mg) were dissolved in freshly distilled DMSO (3 mL). After several freeze-pump-thaw cycles, the mixture was then placed in an oil bath preheated to 80 ˚C and stirred for over 24 h. The resulting solution was poured into 500 mL of cooled

methanol to obtain a crude copolymer. The copolymer was purified by reprecipitation in methanol. An orange powder was obtained after the precipitate was dried in a vacuum oven for 24 h. Yield: 60%.



Scheme S3. Synthesis of the polymers.

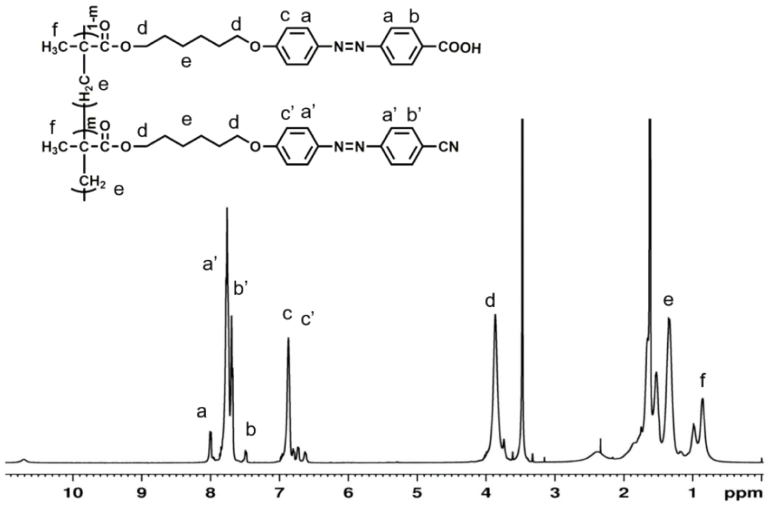


Fig. S4. ^{1}H NMR spectrum of $P_{0.9}$.

Homopolymer P_1. The monomers M_6AZCN (250 mg, 0.64mmol) and AIBN (1wt%, 3mg) were dissolved in freshly distilled anisole (1 mL). After several freeze-pump-thaw cycles, the mixture was then placed in an oil bath preheated to 65 ˚C and stirred for over 24 h. The resulting solution was poured into 500 mL of cooled methanol to obtain a crude homopolymer. The homopolymer was purified by reprecipitation in methanol. An orange powder was obtained after the precipitate was dried in a vacuum oven for 24 h. Yield: 70%.

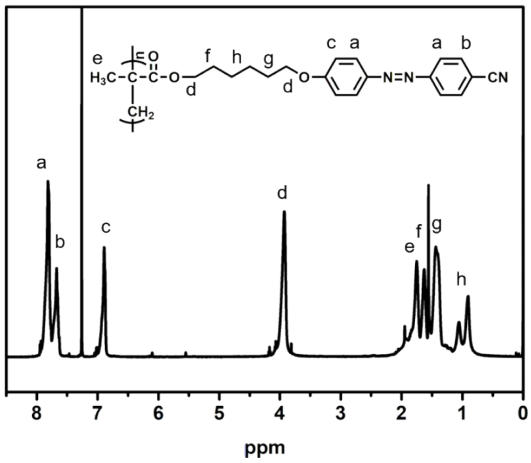


Fig. S5. ^{1}H NMR spectrum of P_1.

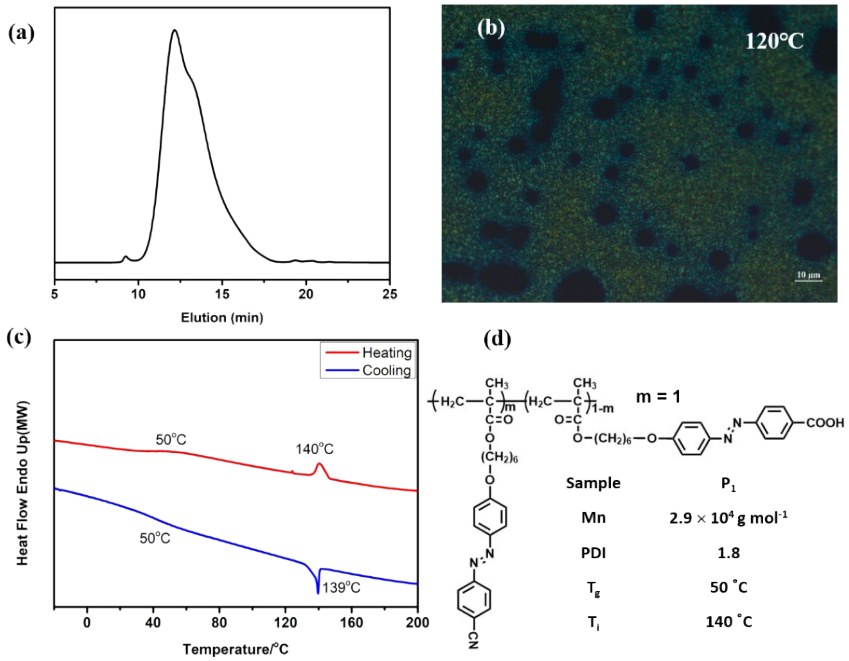


Fig. S6. (a) GPC curve of P_1, (b) POM picture of P_1, (c) DSC curves of P_1, (d) Chemical structure and thermal properties of P_1.

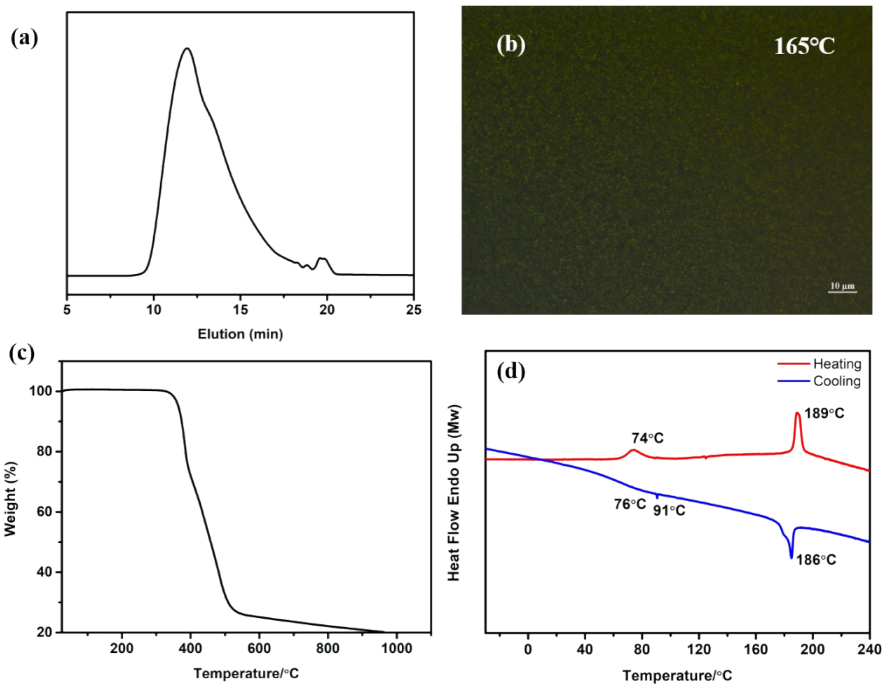


Fig. S7. (a) GPC curve of $P_{0.9}$, (b) POM picture of $P_{0.9}$, (c) TGA curve of $P_{0.9}$, (d) DSC curves of $P_{0.9}$.

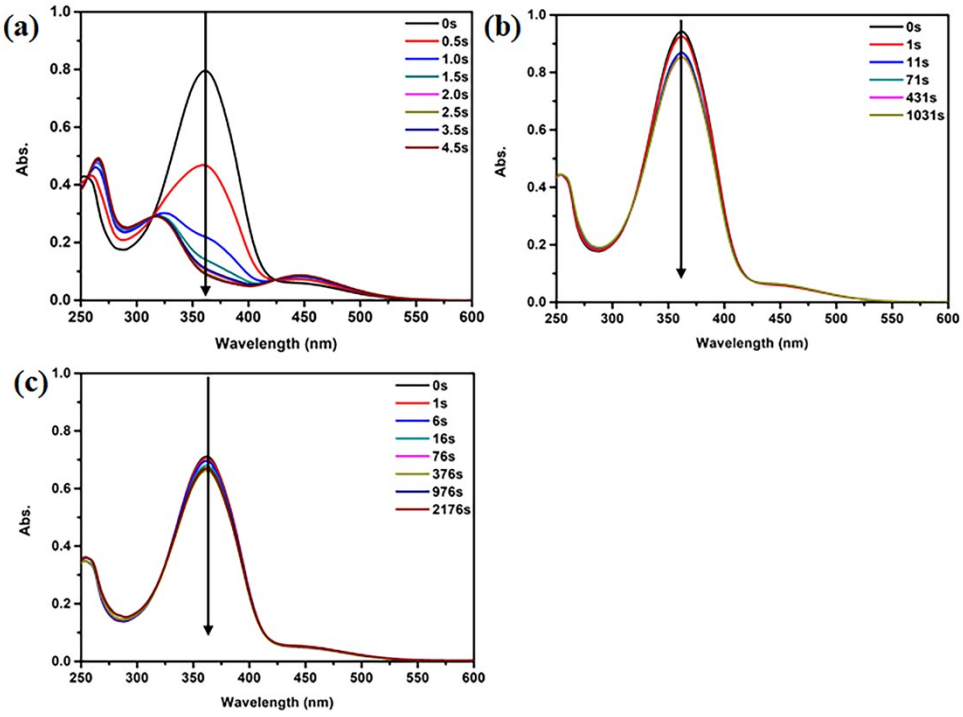


Fig. S8. UV-vis spectrum of $P_{0.9}$ in tetrahydrofuran (THF) irradiated by 365 nm (a), 460 nm (b), 530 nm (c) light at 100 mW cm^{-2}.

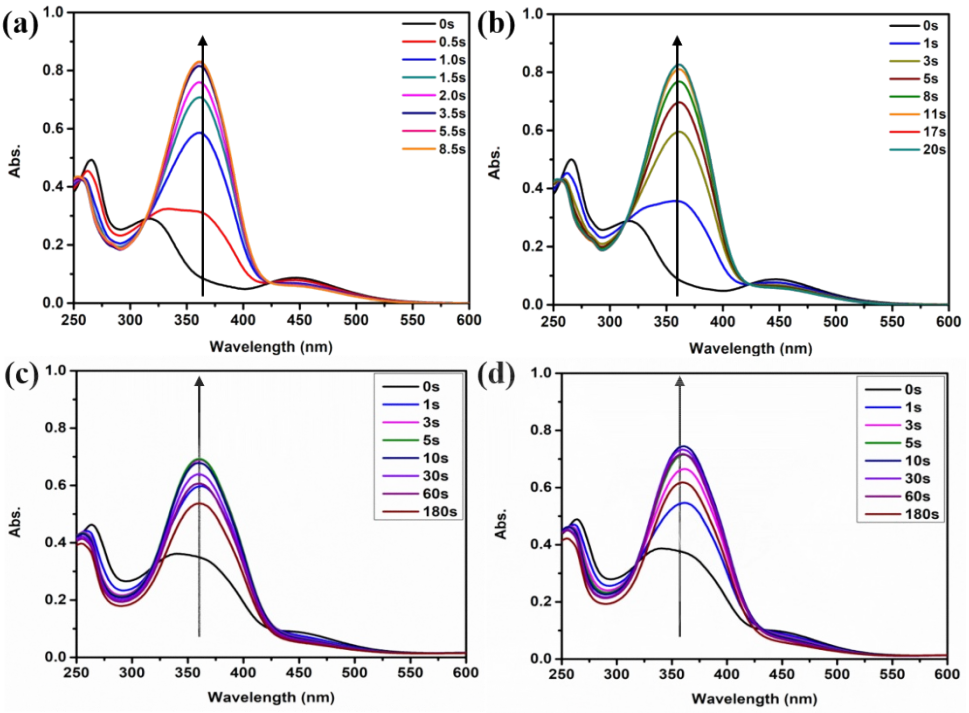


Fig. S9. UV-vis spectrum for reversion process of $P_{0.9}$ irradiated by 460 nm (a), 530 nm (b) light in tetrahydrofuran (THF) and 460 nm (c), 530 nm (d) light in film state at 100 mW cm^{-2} after 365 nm light irradiation.

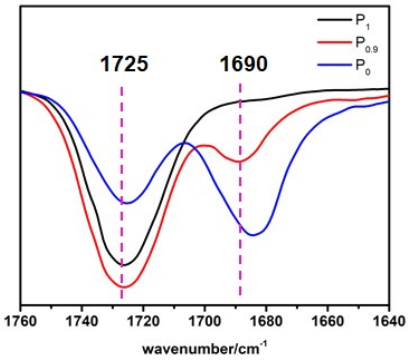
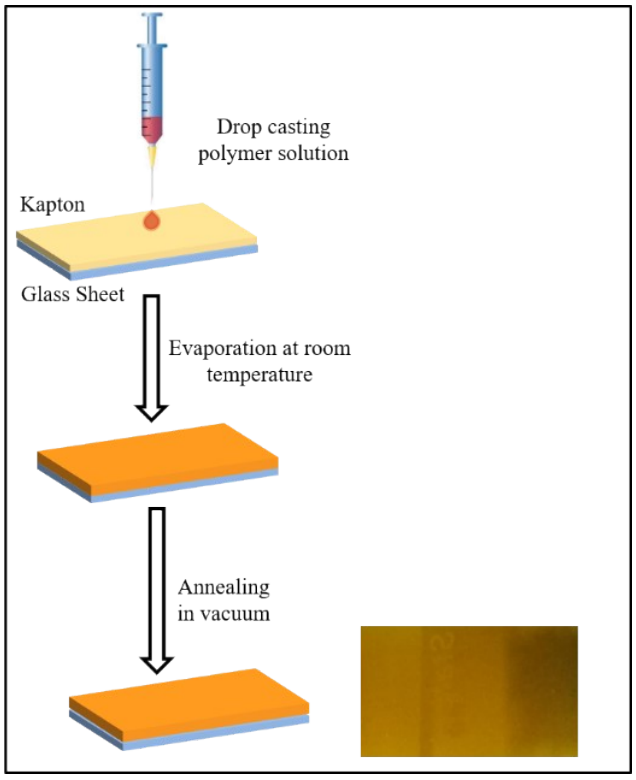


Fig. S10. FTIR spectrum of the homopolymer P_1 (polymerized by monomer M_6AzCN), copolymer $P_{0.9}$, homopolymer P_0 (polymerized by monomer $M_6AzCOOH$).



Scheme S4. Fabrication process of the bilayer film.

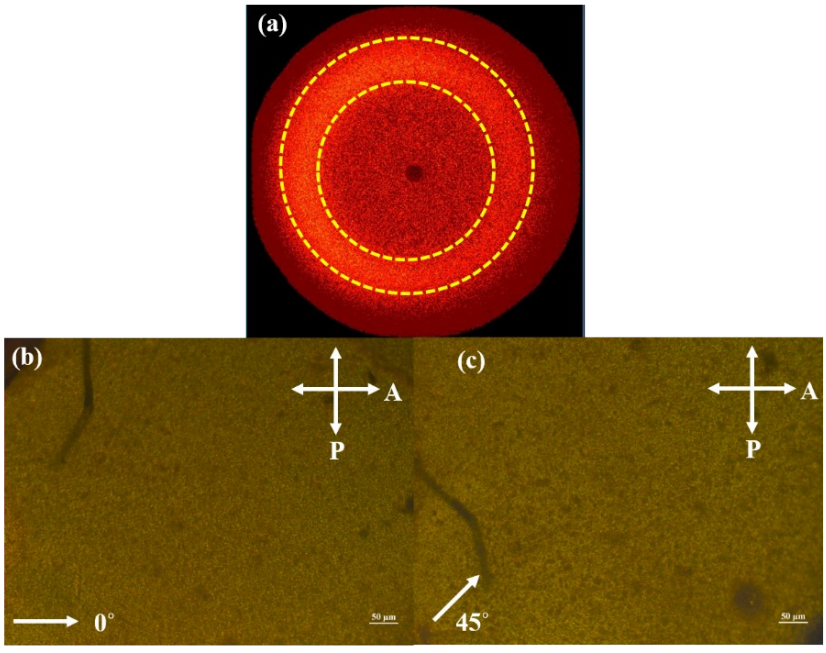


Fig. S11. (a) 2D XRD results for the bilayer film containing $P_{0.9}$. POM pictures (b) and (c) for the bilayer films containing $P_{0.9}$ after annealing. White solid arrows represent the transmission axes of the polarizer (P) and analyzer (A), the sample angle to the analyzer: θ= 0˚, θ= 45˚, respectively.

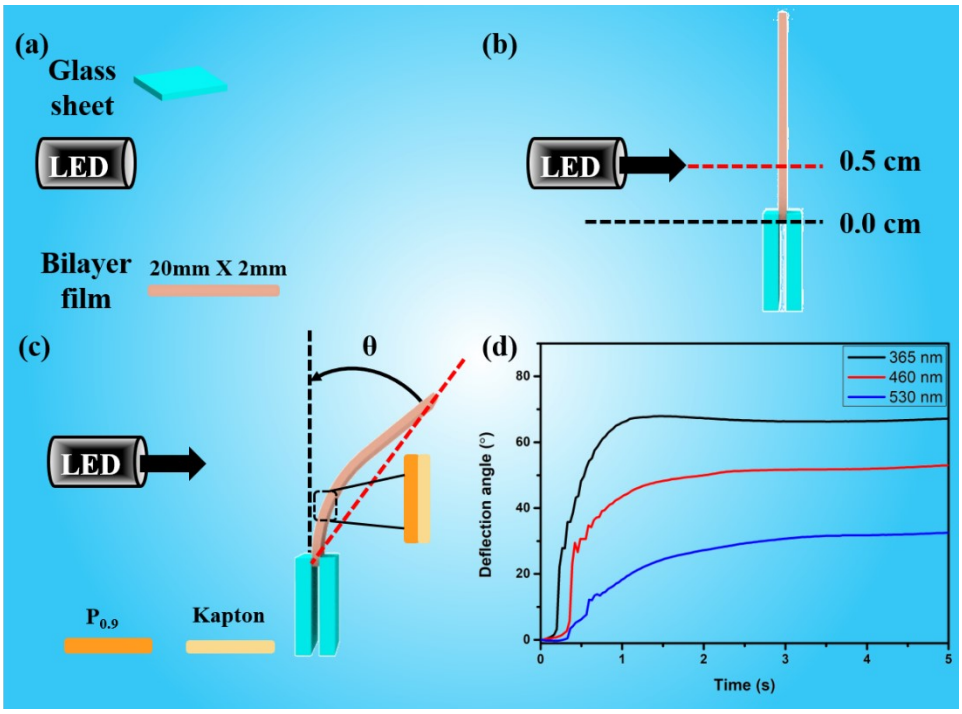


Fig. S12. Materials (a) and scheme (b) of optical setup for photomechanical experiments. (c) Light shined on the photoactive polymer side. (d) Photomechanical behavior for the bilayer strip containing the copolymer $P_{0.9}$ illuminated respectively by 365 nm, 460 nm and 530 nm light at 100 mW cm^{-2} from the AZ-containing polymer side.

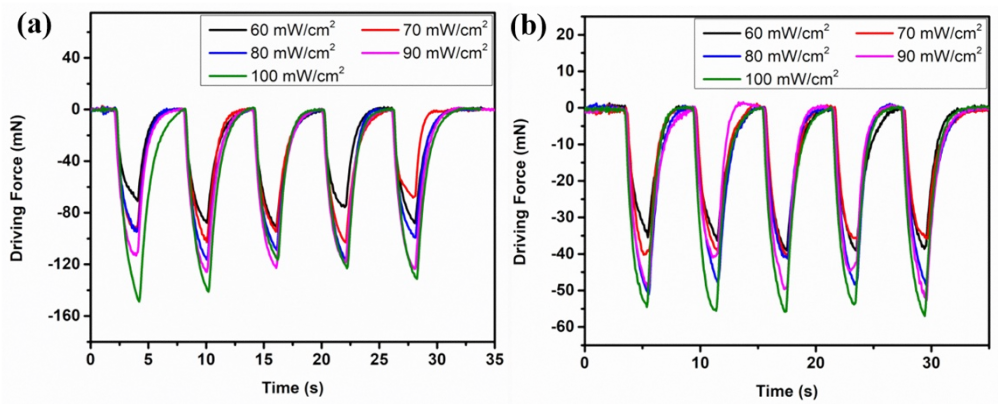


Fig. S13. Driven force of the bilayer films containing $P_{0.9}$ (a) and P_1 (b) under 365 nm light irradiation, which was measured in-situ with a test machine.

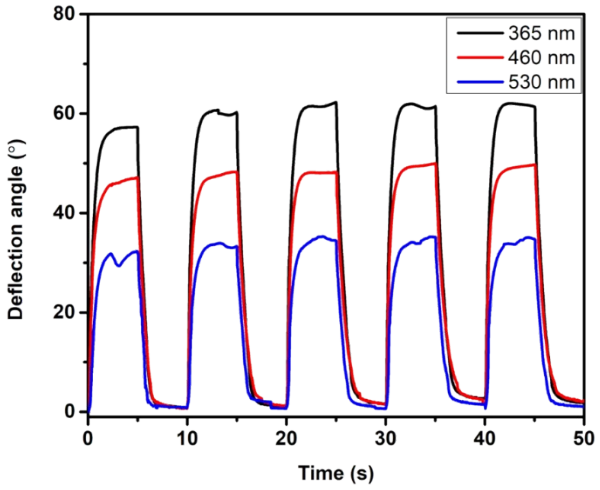
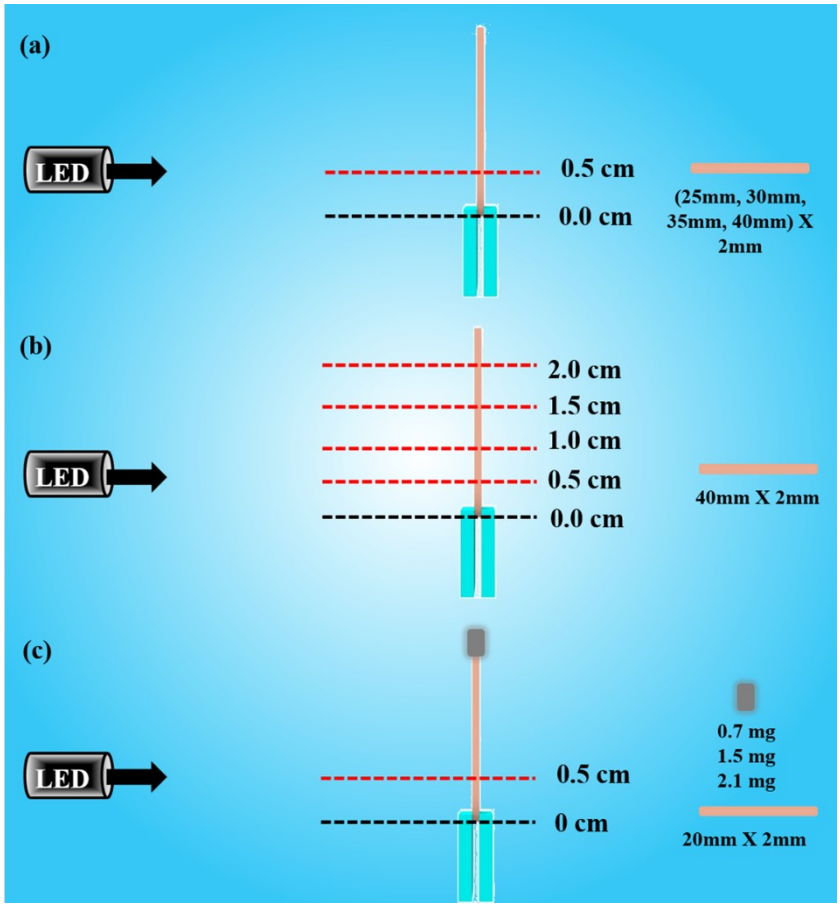


Fig. S14. The photomechanical behaviour of the bilayer strip as turning on and off the 365 nm, 460 nm and 530 nm light at 100 mW cm^{-2}, respectively.



Scheme S5. The photomechanical behaviour of the bilayer strip was modulated by changing the length of the strip (a), the light-irradiated position (b), and the attached different amounts of scotch tape on the end of the actuator (c), respectively, when other conditions are fixed.

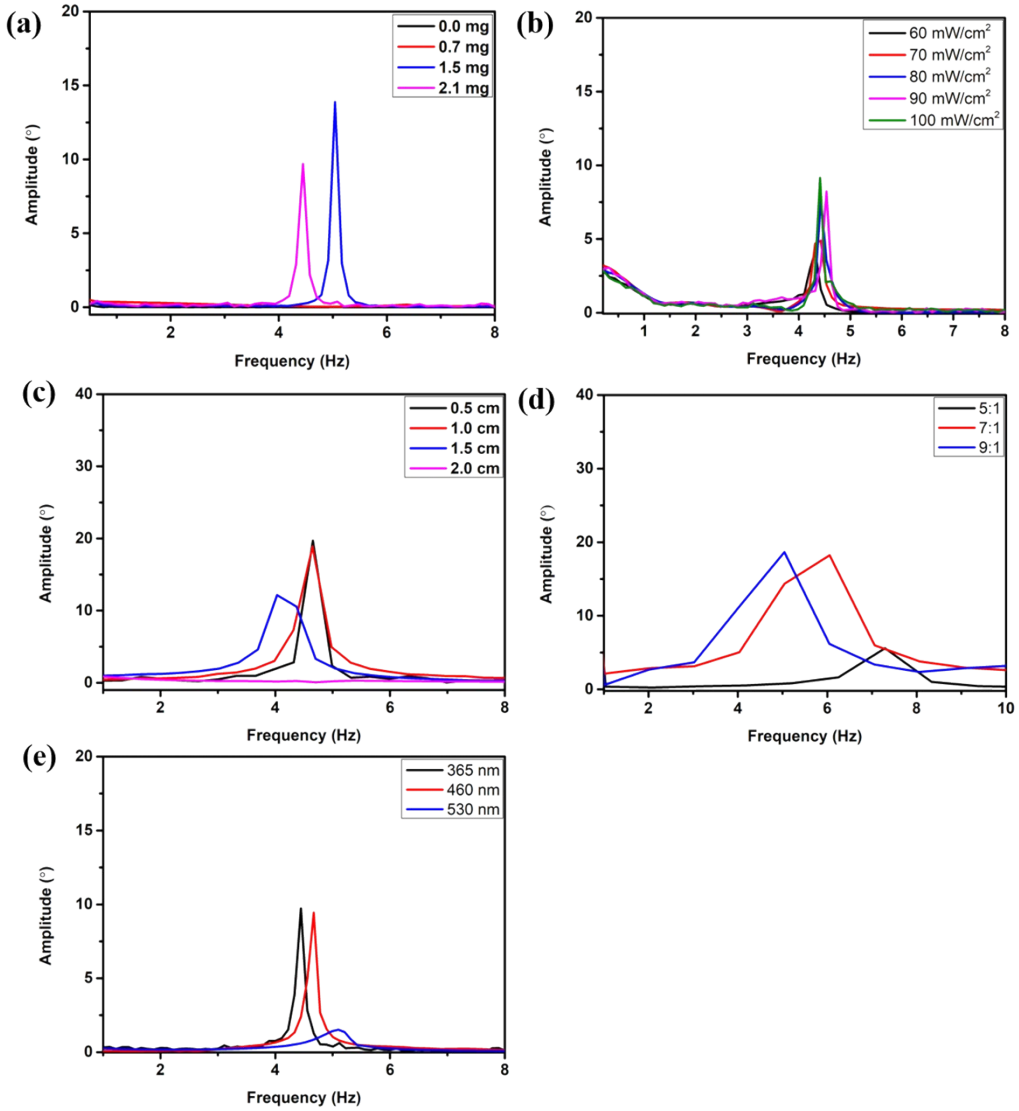


Fig. S15. The frequency and amplitude of the self-oscillator with (a) different amounts of attached scotch tape, (b) different light intensities of 365 nm light, (c) different light-irradiated position under 365 nm light at 100 mw cm^{-2}, (d) different aspect ratios of film, (e) actinic light at 365 nm, 460 nm and 530 nm light (100 mW cm^{-2}).

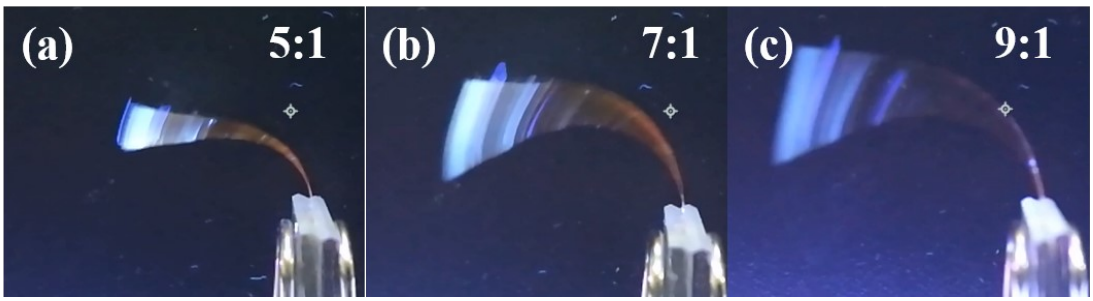


Fig. S16. Snapshots of displacement of self-oscillators with different aspect ratios.

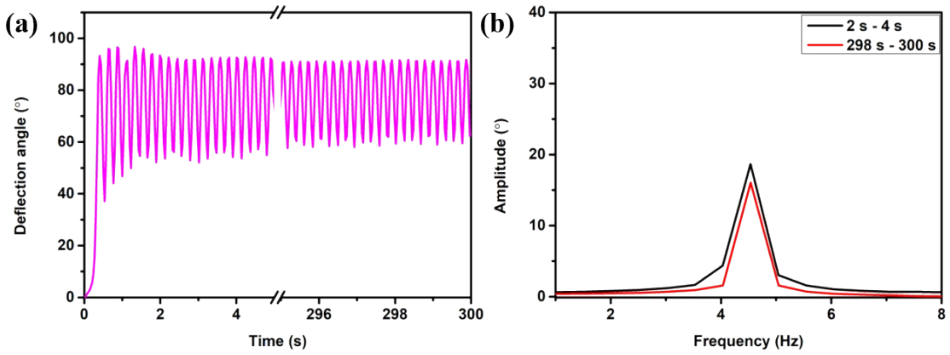


Fig. S17. (a) Self-sustained oscillation of the oscillator under 365 nm light irradiation at 100 mW cm^{-2}. (b) The oscillating frequency and amplitude for the strip during 2s-4s and 298s-300s.

Supporting Movies

Movie S1. Photomechanical behavior of the $P_{0.9}$/Kapton bilayer strip with 365 nm, 460 nm or 530 nm light illumination at 100 mW cm^{-2} from both sides (MP4)

Movie S2. Photomechanical behavior of the P_1/Kapton bilayer strip with 365 nm light illumination at 100 mW cm^{-2} from both sides (MP4).

Movie S3. The $P_{0.9}$/Kapton bilayer strip floated upward during 365 nm, 460 nm or 530 nm light irradiation and sunk after removal of light (MP4).

Movie S4. The self-oscillating behavior of the $P_{0.9}$/Kapton bilayer strip with 365 nm light illumination at 100 mW cm^{-2} (MP4).

Movie S5. The self-oscillating behavior of the $P_{0.9}$/Kapton bilayer strip with 460 nm light illumination at 100 mW cm^{-2} (MP4).

Movie S6. The self-oscillating behavior of the $P_{0.9}$/Kapton bilayer strip with 530 nm light illumination at 100 mW cm^{-2} (MP4).

Movie S7. The self-oscillating behavior of the $P_{0.9}$/Kapton bilayer strip with 365 nm light illumination at 100 mW cm^{-2}, under the condition that both of the capsule and the actuator uncharged, just the capsule charged or both of the capsule and the actuator charged (MP4).

Movie S8. The self-oscillator of the $P_{0.9}$/Kapton bilayer strip for signal transmission under 365 nm light illumination at 100 mW cm^{-2} (MP4).

Supporting References

S1 H. Yu, T. Iyoda, T. Ikeda, *J. Am. Chem. Soc*., 2006, **128**, 11010-11011.

S2 H. Ren, D. Chen, Y. Shi, H. Yu, Z. Fu, *Polym. Chem*., 2015, **6**, 270-277.