Supplementary Information

An iodine-driven muscle-mimicking self-resettable bilayer hydrogel actuator

Kangle Guo, Hao Sun, Mengmeng Nan, Tiedong Sun,* Guangtong Wang,* and Shaoqin Liu*

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1. Supplemental Experimental Procedures

1.1 Material and Instruments

1.1.1 Material. Polyethylene glycol diacrylate (M_w = 10000, > 95 %) was purchased from Shenzhen Meiluo Technology Co., Ltd. Hydroxypropyl acrylate (HPA, > 80.0 %) and 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (HHEMPP, ≥ 98.0 %) were purchased from Aladdin Reagent Co., Ltd. 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS, 98 %) was purchased from InnoChem. Acetic acid (≥ 99.5 %) was purchased from Tianjin Tianli Chemical Reagent Co., Ltd. KI $NaIO_3$, $CS(NH_2)_2$, and other compounds were purchased from Beijing J&K Scientific. All reagents are analytical grade reagents and are used without further purification.

1.1.2 Instruments. The infrared spectra were obtained by Nicolet is5003190721 spectrometer. Photogragh was captured by a Canon EOS 550D camera. Scanning electron microscope (SEM) images were obtained by TESCAN AMBER, Czech Republic. UV-Vis spectra were measured by a HITACHI U-4100 spectrophotometer. Compress modulus and Young's modulus were calculated by the stress-strain graphs obtained by a SASTest CMT2103 universal testing machine. Contact angel was determined by a KSV CAM101 optical goniometer. The thermogravimetric analysis was conducted by a Netzsch STA449F3.

1.2 Synthesis

1.2.1 Synthesis of PEGDA hydrogel. The PEGDA hydrogel was synthesized by photoinduced free radical PEGDA. 94.24 mg PEGDA, and 1 mg HHEMPP, the photoinitiator, were dissolved in about 2 mL of deionized water. The mixture was transferred to a polytetrafluoroethylene mold and irradiated by 395 nm ultraviolet light for 3 minutes, yielding the PEGDA hydrogel. To prepare the PEGDA hydrogel with various wt% of PEGDA, the mass of PEGDA added was changed. The yielded hydrogel was immersed in PBS buffer for full swelling.

1.2.2 Synthesis of PEGDA-PHPA-PAMPS bilayer hydrogel actuator. The PHPA-PAMS layer was first synthesized in a polytetrafluoroethylene mold. An aqueous solution containing 3.93 M HPA, 78.6 mM AMPS, and 0.5 mg/mL^{-1} HHEMPP was added into the mold, and then irradiated by 395 nm ultraviolet light for 3 min. Before the entire solidification of the PHPA-PAMS layer. 4.5 wt% polyethylene glycol diacrylate aqueous solution was added. The solution was continuously irradiated

by 395 nm UV light for 5 min. yielding the bilayer hydrogel, PEGDA-PHPA-PAMPS. The bilayer hydrogel was immersed in pH 7.1 PBS buffer for full swelling.

1.3 I_2-responsiveness of PEGDA hydrogel

A 10 mm× 10 mm piece of PEGDA hydrogel was immersed in 14.4 mL aqueous solution containing 69.4 mM KI and 100 mM acetic acid until it fully swelled. 0.6 mL, 200 mM $NaIO_3$ solution was added to yield I_2. The size change of the hydrogel was measured by graph paper. The change of mechanical strength of PEGDA hydrogel was measured by the SASTest CMT2103 universal testing machine. The change of contact angle was measured by the KSV CAM101 optical goniometer. 0.72 mL, 400 mM $CS(NH_2)_2$ solution was used to eliminate the I_2 for restoring the PEGDA hydrogel. The I_2-responsive deswell-swell cycle was conducted at least 3 times by alternately adding the equal equivalent of $CS(NH_2)_2$ and $NaIO_3$.

1.4 Self-resettable deswelling of PEGDA hydrogel

A 10 mm × 10 mm piece of PEGDA hydrogel was immersed in 13.74 mL aqueous solution containing 72.8 mM KI and 100 mM acetic acid until it fully swelled. A 1.26 mL mixed solution containing 95.2 mM $NaIO_3$ and 209.5 mM $CS(NH_2)_2$ was added. Hence the initial concentrations, $[KI]_0$ = 66.7 mM, [acetic acid]$_0$ = 100 mM, $[NaIO_3]_0$ = 8.0 mM, $[CS(NH_2)_2]_0$ = 17.6 mM. The time-dependent size change of the hydrogel was recorded. The change in I_2 concentration was monitored by the UV-Vis absorbance of the solution at 475 nm. To alter the I_2 concentration, the concentration of $NaIO_3$ and $CS(NH_2)_2$ in the mixed solution is changed.

1.5 Self-resettable curvature reverse of PHPA-PAMPS-PEGDA bilayer hydrogel actuator

PHPA-PAMPS-PEGDA bilayer hydrogel actuator was immersed in 18.32 mL aqueous solution containing 72.8 mM KI and 100 mM acetic acid until it fully swelled. A 1.68 mL mixed solution containing 95.2 mM $NaIO_3$ and 209.5 mM $CS(NH_2)_2$ was added. Hence the initial concentrations, $[KI]_0$ = 66.7 mM, [acetic acid]$_0$ = 100 mM, $[NaIO_3]_0$ = 8.0 mM, $[CS(NH_2)_2]_0$ = 17.6 mM. The time-dependent curvature change of the hydrogel was recorded. The change of I_2 concentration was monitored by the UV-Vis absorbance of the solution at 475 nm. For altering the I_2 concentration, the concentration of $NaIO_3$ and $CS(NH_2)_2$ in the mixed solution is changed.

2. Supplemental Figures

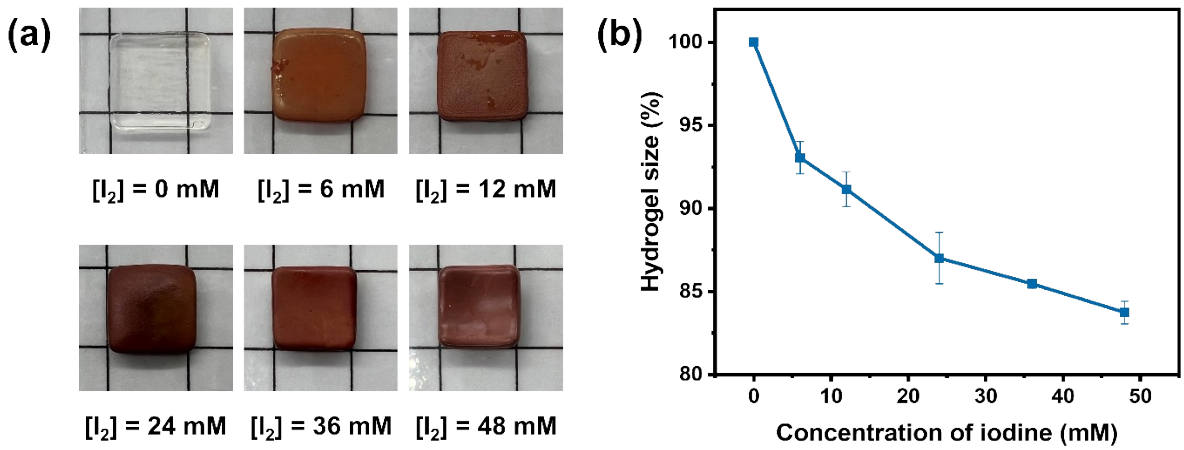

Figure S1. The shrinkage and discoloration of PEGDA hydrogel result from the addition of different concentrations of I_2.

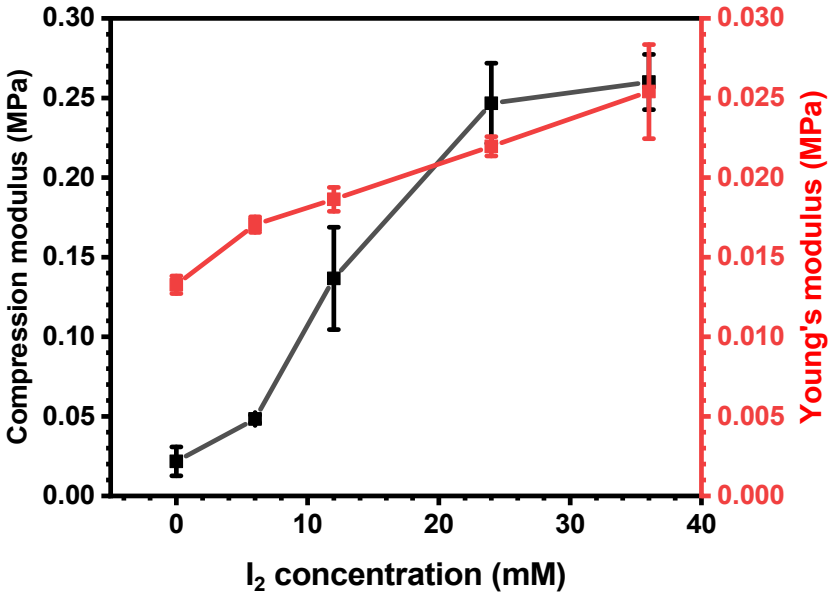

Figure S2. The increase of stiffness of the PEGDA hydrogel with the addition of I_2.

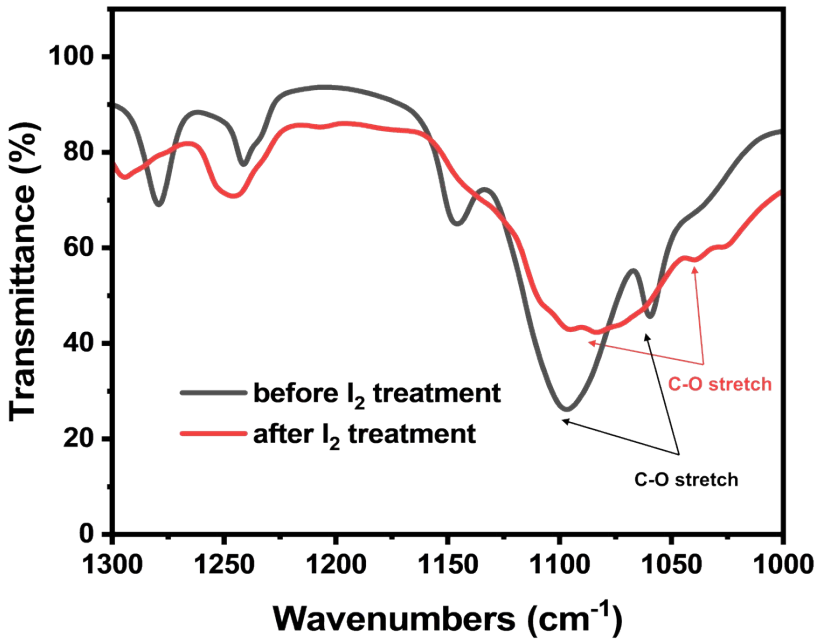

Figure S3. The FTIR spectra of the PEGDAs before (black) and after (red) the treatment by I_2.

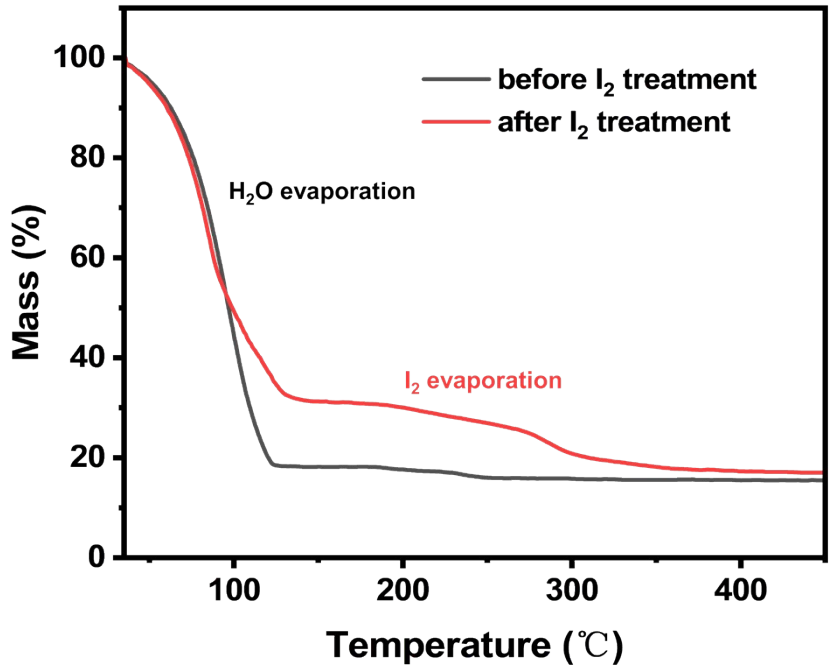

Figure S4. The thermogravimetric analysis of the PEGDAs before (black) and after (red) the treatment by I_2.

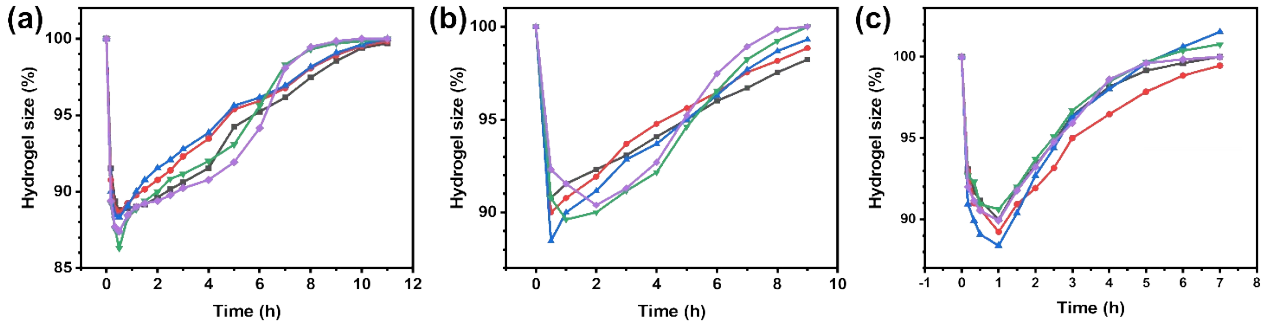

Figure S5. The self-resettable changes in the size of PEGDA hydrogel. T = 293 K. The initial concentrations of the reactants in the reaction mixture. $[KI]_0$ = 66.7 mM, [acetic acid]$_0$ = 100 mM. (a) Black: $[NaIO_3]_0$ = 2.5 mM, $[CS(NH_2)_2]_0$ = 5.0 mM, red: $[NaIO_3]_0$ = 5.0 mM, $[CS(NH_2)_2]_0$ = 10.0 mM, sky blue: $[NaIO_3]_0$ = 7.5 mM, $[CS(NH_2)_2]_0$ = 15.0 mM, green: $[NaIO_3]_0$ = 10.0 mM, $[CS(NH_2)_2]_0$ = 20.0 mM, purple: $[NaIO_3]_0$ = 12.5 mM, $[CS(NH_2)_2]_0$ = 25.0 mM. (b) Black: $[NaIO_3]_0$ = 2.5 mM, $[CS(NH_2)_2]_0$ = 5.5 mM, red: $[NaIO_3]_0$ = 5.0 mM, $[CS(NH_2)_2]_0$ = 11.0 mM, sky blue: $[NaIO_3]_0$ = 7.5 mM, $[CS(NH_2)_2]_0$ = 16.5 mM, green: $[NaIO_3]_0$ = 10.0 mM, $[CS(NH_2)_2]_0$ = 22.0 mM, purple: $[NaIO_3]_0$ = 12.5 mM, $[CS(NH_2)_2]_0$ = 27.5 mM. (c) Black: $[NaIO_3]_0$ = 2.5 mM, $[CS(NH_2)_2]_0$ = 6.0 mM, red: $[NaIO_3]_0$ = 5.0 mM, $[CS(NH_2)_2]_0$ = 12.0 mM, sky blue: $[NaIO_3]_0$ = 7.5 mM, $[CS(NH_2)_2]_0$ = 18.0 mM, green: $[NaIO_3]_0$ = 10.0 mM, $[CS(NH_2)_2]_0$ = 24.0 mM, purple: $[NaIO_3]_0$ = 12.5 mM, $[CS(NH_2)_2]_0$ = 30.0 mM.

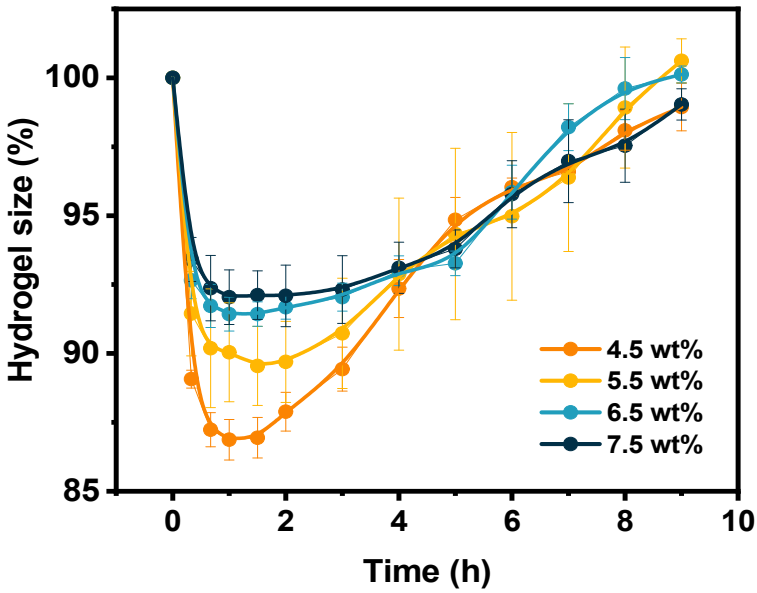

Figure S6. The I_2-driven temporary deswelling of different PEGDA hydrogels. T = 298 K. The initial concentrations of the reactants, $[KI]_0$ = 66.7 mM, [acetic acid]$_0$ = 100 mM, $[NaIO_3]_0$ = 12.0 mM, $[CS(NH_2)_2]_0$ = 28.8 mM. Orange: PEGDA hydrogel synthesized from 4.5 wt% monomer solution. Yellow: PEGDA hydrogel synthesized from 5.5 wt% monomer solution. Sky blue: PEGDA hydrogel synthesized from 6.5 wt% monomer solution. Dark blue: PEGDA hydrogel synthesized from 7.5 wt% monomer solution.

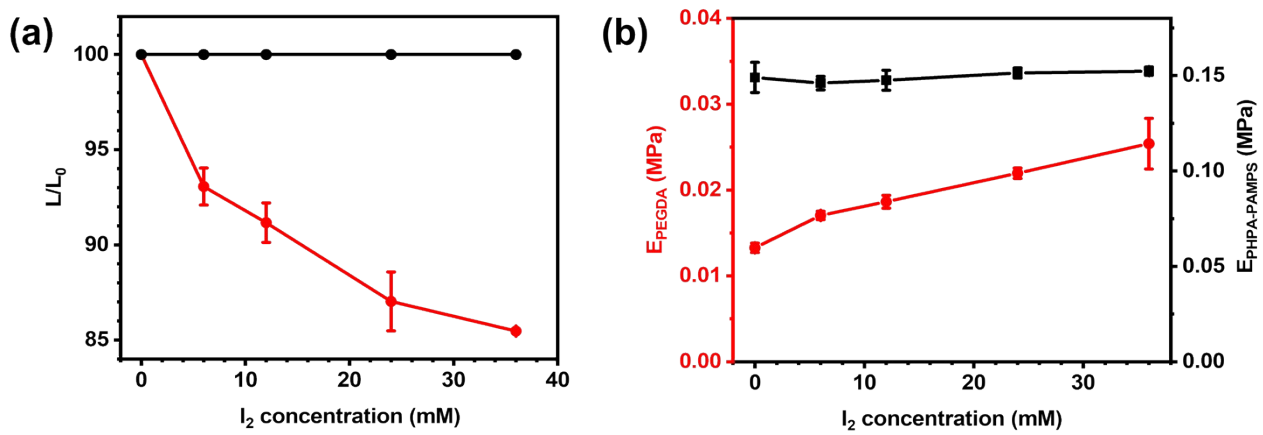

Figure S7. (a) The change of shrinkage ratio of PHPA-PAMPS layer (black) and PEGDA layer (red) with the increase of I_2 concentration. (b) The change of Young's moduli of PHPA-PAMPS layer (black) and PEGDA layer (red) with the increase of I_2 concentration.

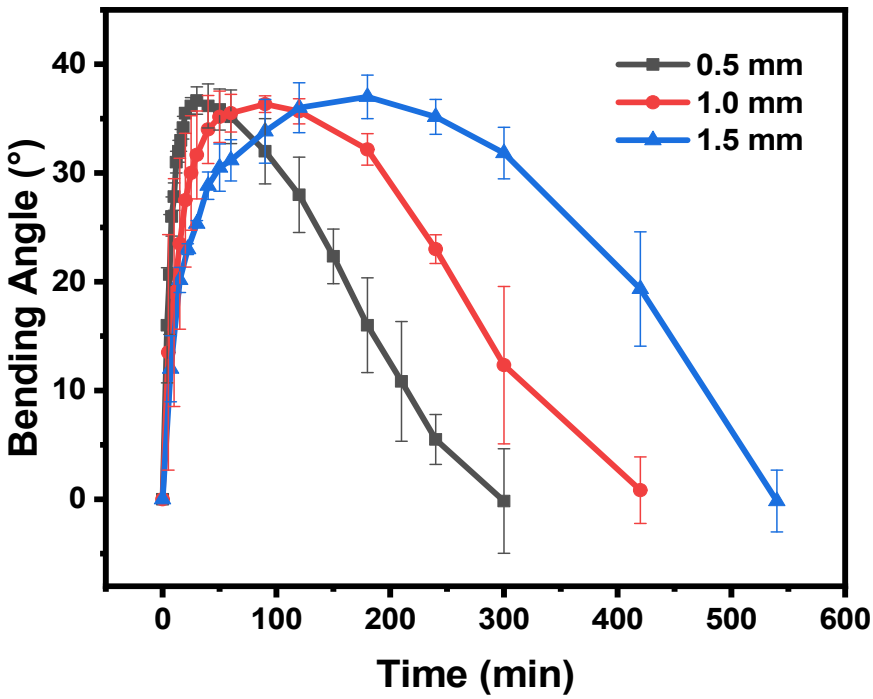

Figure S8. The I_2-driven self-resettable bending of the bilayer hydrogel actuator with different PEGDA layer thicknesses. T = 298 K. The initial concentrations of the reactants, $[KI]_0$ = 66.7 mM, $[\text{acetic acid}]_0$ = 100 mM, $[NaIO_3]_0$ = 5.0 mM, $[CS(NH_2)_2]_0$ = 11.0 mM.

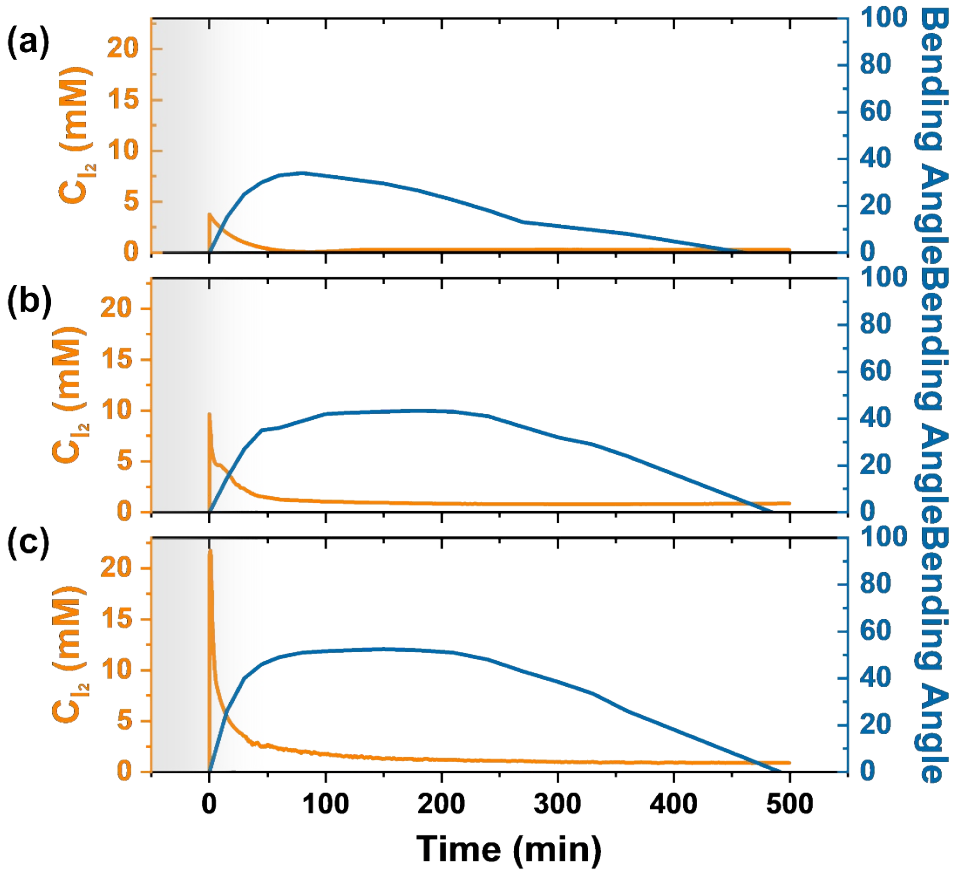

Figure S9. The I_2-driven temporary reversal of the bilayer actuator. T = 298 K. The initial concentrations of the reactants, $[KI]_0$ = 66.7 mM, [acetic acid]$_0$ = 100 mM. (a) $[NaIO_3]_0$ = 2.0 mM, $[CS(NH_2)_2]_0$ = 4.4 mM. (b) $[NaIO_3]_0$ = 5.0 mM, $[CS(NH_2)_2]_0$ = 11.0 mM. (c) $[NaIO_3]_0$ = 8.0 mM, $[CS(NH_2)_2]_0$ = 17.6 mM.