Supporting Information for RSC Advances

Photomechanical Bending of Linear Azobenzene Polymer

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1. Materials

The starting polymer poly[oxy(methylsilylene)] (PHMS) was purchased from GELEST.INC. The molecule weight of PHMS was 2200~2400 g/mol, and the polydispersity (PDI = 2.0) of PHMS was obtained by GPC. The chloroplatinic acid catalyst (H_2PtCl_6) was brought from Tokyo Chemical Industry Co., LTD. NaH (Aldrich, 60%) were used as received. The dry toluene was obtained by vacuum distillation. All other solvents were analytical grade and used as received without further purification.

2. Characterization

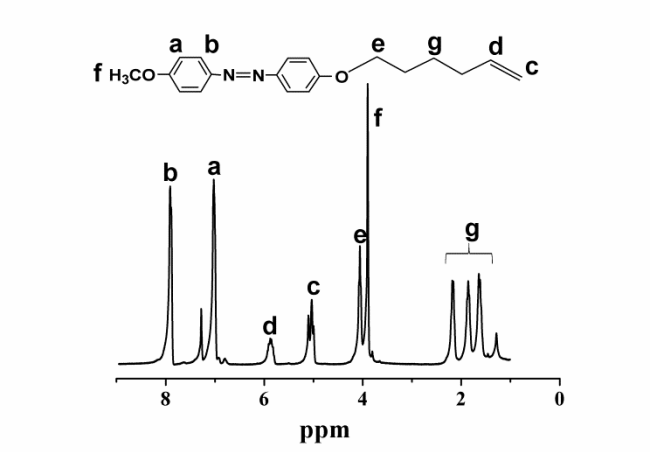

Figure S1. ^{1}H NMR spectrum of 1-(4-(hex-5-enyloxy)phenyl)-2-phenyldiazene in $CDCl_3$ solvent.

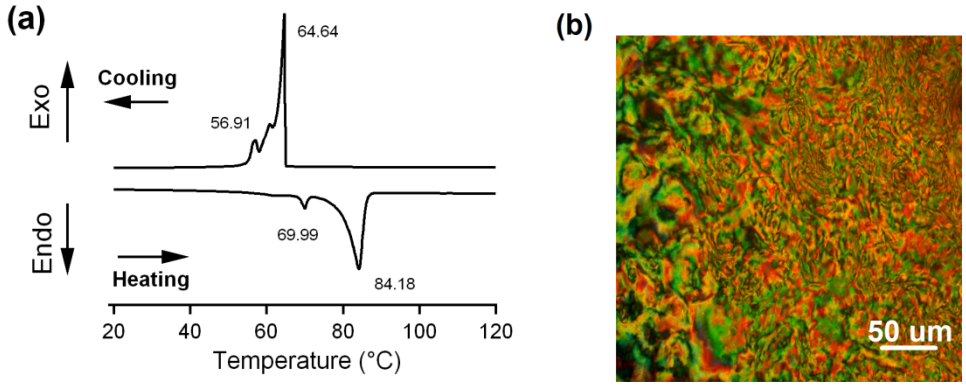

Figure S2. (a) DSC curve of 1-(4-(hex-5-enyloxy)phenyl)-2-phenyldiazene. (b) POM of 1-(4-(hex-5-enyloxy)phenyl)-2-phenyldiazene at 78°C with a magnification of 20 multiple.

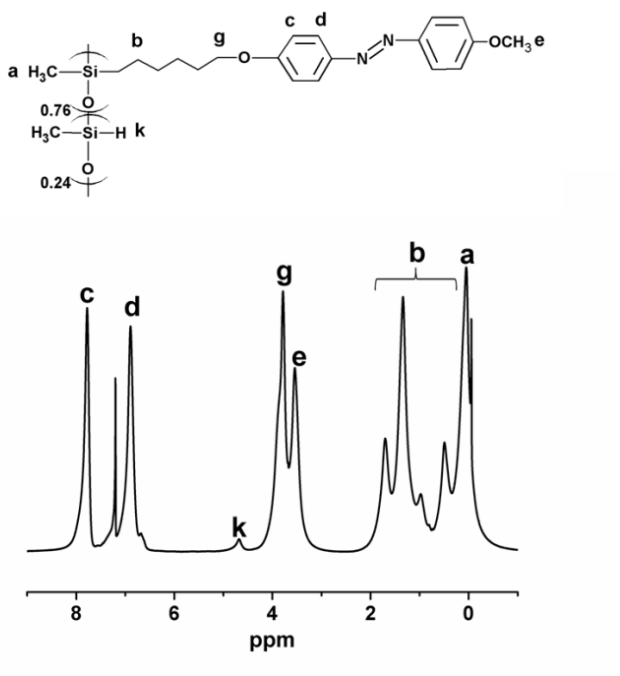

Figure S3. ^{1}H NMR spectrum of azobenzene polymer, PsAzo.

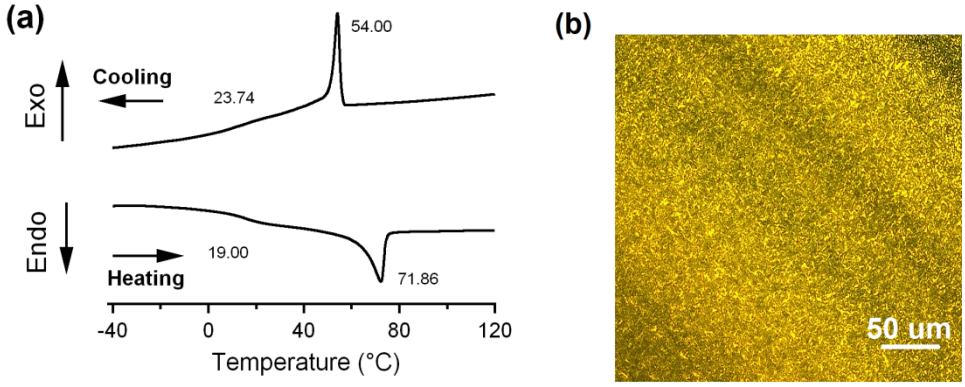

Figure S4. (a) DSC curve of the PsAzo. (b) POM image of the PsAzo at room temperature with a magnification of 20 multiple.

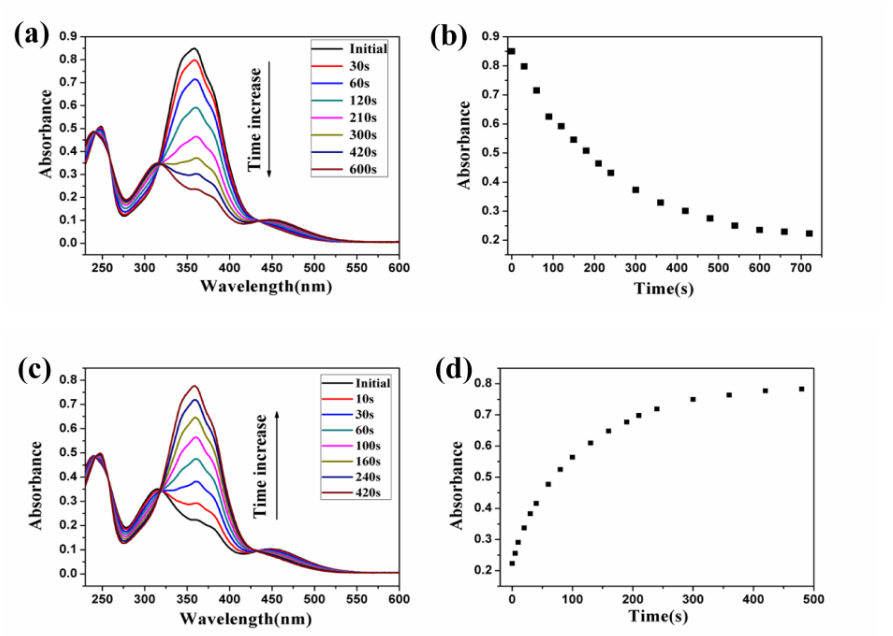

Figure S5. The gradual transitions of the UV (365 nm, 0.5 mW/cm^2) / Visible (>425 nm, 100 mW/cm^2) absorption spectra of a PsAzo on a quartz substrate under UV (a and b) and visible light (c and d) irradiation.

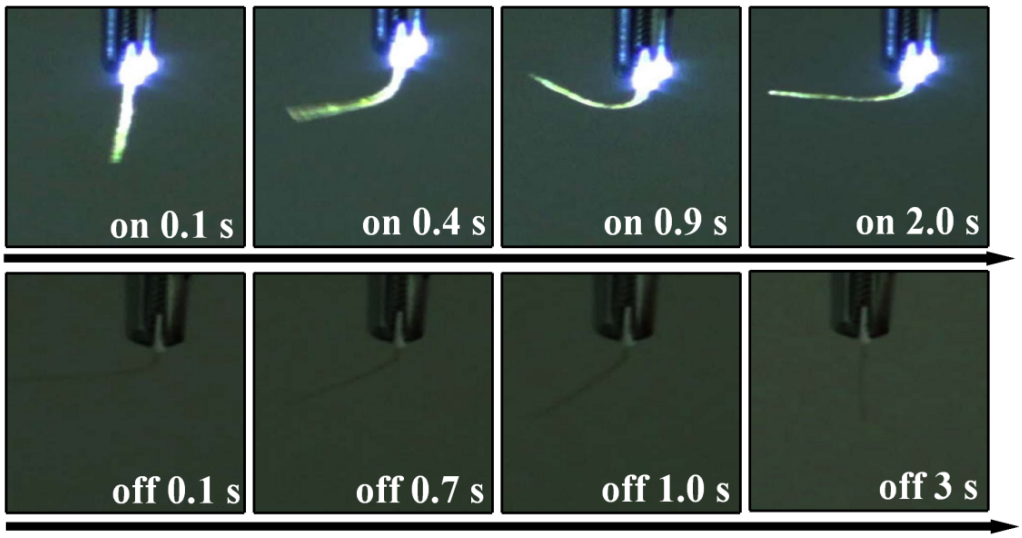

Figure S6. The process of reversible bending of SFA actuators (2 mm × 12 mm × 16 μm) alternate controlled with UV light (365 nm, 70 mW/cm^2).

3 Preparation of silk fibroin solution

The 10 g cocoons were placed in the 1000 ml water with 0.06 g Na_2CO_3 boiling for 40 min, then rinsed thoroughly with water to extract the glue-like sericin proteins and dried in the oven[1,2]. To completely extract the sericin proteins, this process had to be repeated for six times. Then 1 g extracted silk was dissolved in the 10 ml mixed solution with ethyl alcohol (6.14 ml), and water (7.2 mL), calcium chloride (5.54 g) at 72 ^oC for 1 h. The high concentration silk fibroin solution was dialyzed using slide-a-lyzer dialysis cassettes (MWCO 3500, Pierce) at room temperature for 5 days to remove $CaCl_2$ and ions presented in the fibroin[3]. The dialysate was centrifuged at 0 ^oC for 40 min and then was filtrated to remove impurities and aggregates. The finally concentration of the silk fibroin solution was 3 wt% which decided by weighing remain solid silk after drying.

4 Preparation of silk fibroin-azobenzene polymer (SFA) actuators

The 6 wt% PDMS in toluene solution was casted on the cut glass slide (2.5 × 2.5 mm) at the speed of 2000 rpm, then it was taken to the hot stage to cross-link at 90 ^oC for 1 hour. PDMS surfaces which washed with 70% ethanol solution and rinsed three times with distilled H_2O were used to form the free-standing silk films. The 3 wt% silk fibroin solution of 800 μl was cast on the PDMS surface for 24 h at room temperature. The films were taken to the vacuum oven for 48 h to complete drying. In the end, the PsAzo solution-spinning (8 wt%, PsAzo was dissolved in toluene) was applied to form the robust SFA actuator. All the procedures were carried out in the clean-room.

5 References

1 R. Valluzzi, S. P. Gido, *Biopolymers* 1997, **42**, 705.

2 R. Valluzzi, S. P. Gido, W. P. Zhang, W. S. Muller, D.L. Kaplan, *Macromolecules* 1996, **29**, 8606.

3 M. Hernandez-Velez, *Thin Sol. Films* 2005, **495**, 51.