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Supporting Information

Supramolecular hydrogen-bonded photodriven actuators based on an azobenzene-containing main-chain liquid crystalline poly(ester-amide)

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Characterization

^{1}H NMR spectra were recorded on a Bruker Avance III 400 MHz NMR spectrometer. Thermogravimetric analysis (TGA) was performed on a Netzsch TG 209 instrument in a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Differential scanning calorimeter (DSC, Netzsch 200 F3) was used to study the phase transitions of the azo polymer at a heating/cooling rate of 10 °C min^{-1} under nitrogen. The temperature and heat flow scale were calibrated with standard materials including indium (70-190 °C), tin (150-270 °C), zinc (350-450 °C), bismuth (190-310 °C), and mercury (-100-0 °C) in different temperature ranges. The glass transition temperature (T_g) of the azo polymer was determined as the midpoint of the step change of the heat capacity, while the phase transition temperature was measured from the maximum/minimum of the endothermic/exothermic peaks. The liquid crystalline texture of the azo polymer and the alignment state of the polymer fibers were observed by using an Olympus BX51 polarizing optical microscope (POM, with crossed polarizer and analyzer) equipped with a Linksys 32 THMSE600 hot stage and a digital camera (Micropublisher 5.0 RTV). A Bio-Rad FTS6000 FT-IR spectrometer equipped with an UMA-500 microscope, an MCT detector (cooled with liquid nitrogen), and a Linkam FTIR600 hot stage and temperature control system was used to carry out the variable temperature FT-IR measurements. The studied polymer sample was sandwiched between two KBr slides, and its temperature was changed at a rate of 10 °C min^{-1}. Sixteen scans were conducted for each spectrum at the selected temperatures in the wavenumber range of 700-4000 cm^{-1} with a resolution of 8 cm^{-1}. An UV-vis scanning spectrophotometer (TU1900, Beijing Purkinje General Instrument Co., Ltd.) was used to obtain the UV-vis spectra of the studied azo polymer solution and film at 25 °C. The photochemical isomerization of the polymer solution and film was investigated by irradiating them first with a 365 nm UV lamp (12 W) until the photostationary state was reached and then with a 450 nm visible light lamp (18 W, wavelength range 400-550 nm, $\lambda_{\max}$ = 450 nm; a filter was put between the sample and the lamp during the study in order to block the light with wavelength λ < 430 nm).

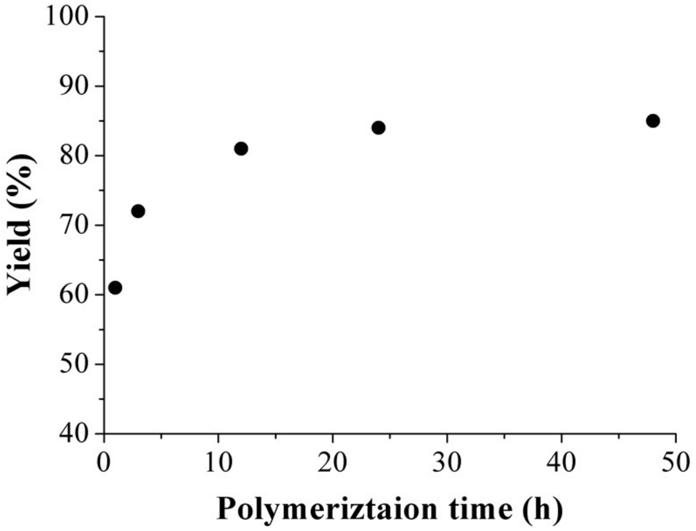


Fig. S1 Dependence of the yields of Azo-PEA-6 on the polymerization time.

The model reaction between Azo-M-6 and *n*-butylamine

To a one-neck round-bottom flask (10 mL) with a magnetic stir bar inside was added Azo-M-6 (49.4 mg, 0.1 mmol), dried DMF (1.5 mL), and dried methanol (0.5 mL) successively. A clear solution was obtained after 5 min of stirring at room temperature. After the above solution was bubbled with argon for 15 min, *n*-butylamine (7.3 mg, 0.1 mmol) and TEA (42 μL, 0.3 mmol) were added. The sealed reaction mixture was magnetically stirred at 40 °C for 7 h (Azo-M-6 proved to be completely reacted, as confirmed by the thin layer chromatography). The reaction mixture was then cooled down to the room temperature and poured into water. The precipitate was collected by filtration and dried at 40 °C under vacuum to the constant weight to provide an orange-yellow product.

Fig. S2 shows the ^{1}H NMR spectrum of the product obtained from the above reaction between Azo-M-6 and *n*-butylamine. The peak (around 2.94 ppm) corresponding to the protons in the *N*-hydroxysuccinimide carboxylate unit of Azo-M-6 (Fig. 1a) completely disappeared in the ^{1}H NMR spectrum of the above product. In addition, no peaks between 2 and 3 ppm (corresponding to the protons of the methylene units around the nitrogen atom in the product obtained by the Michael addition of *n*-butylamine with acrylate group) were discernible in the

^{1}H NMR spectrum of the above product (L. Fang, H. T. Zhang, Z. Li, Y. Zhang, Y. Y. Zhang and H. Zhang, *Macromolecules*, 2013, **46**, 7650). These results clearly demonstrated that the amino group of *n*-butylamine only reacted with the *N*-hydroxysuccinimide carboxylate group of Azo-M-6 instead of its acrylate group under the above reaction condition, thus leading to *N*-butyl 4-((4-(*ω*-acryloyloxyhexyloxy))phenylazo)benzamide (see its chemical structure in Fig. S2).

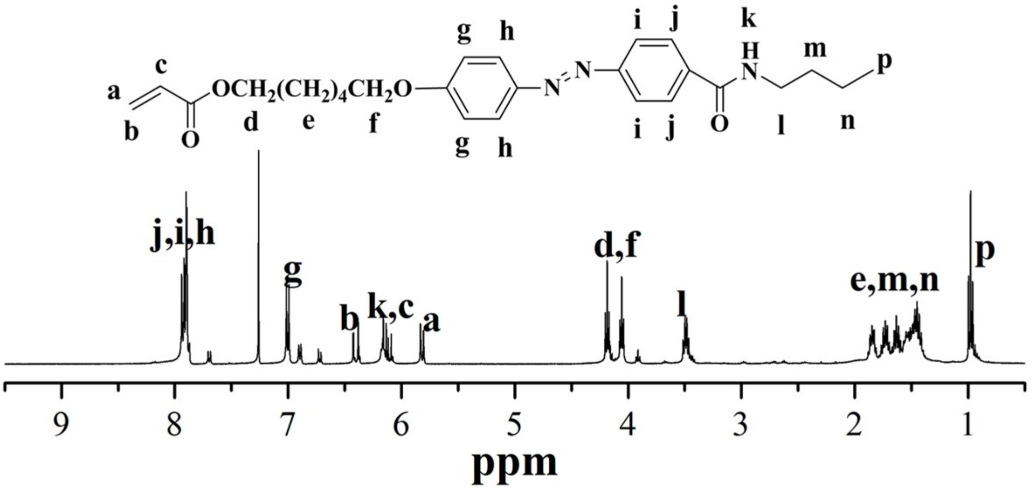


Fig. S2 ^{1}H NMR spectrum of the product obtained from the reaction between Azo-M-6 and *n*-butylamine (i.e., *N*-butyl 4-((4-(*ω*-acryloyloxyhexyloxy))phenylazo)benzamide) in $CDCl_3$.

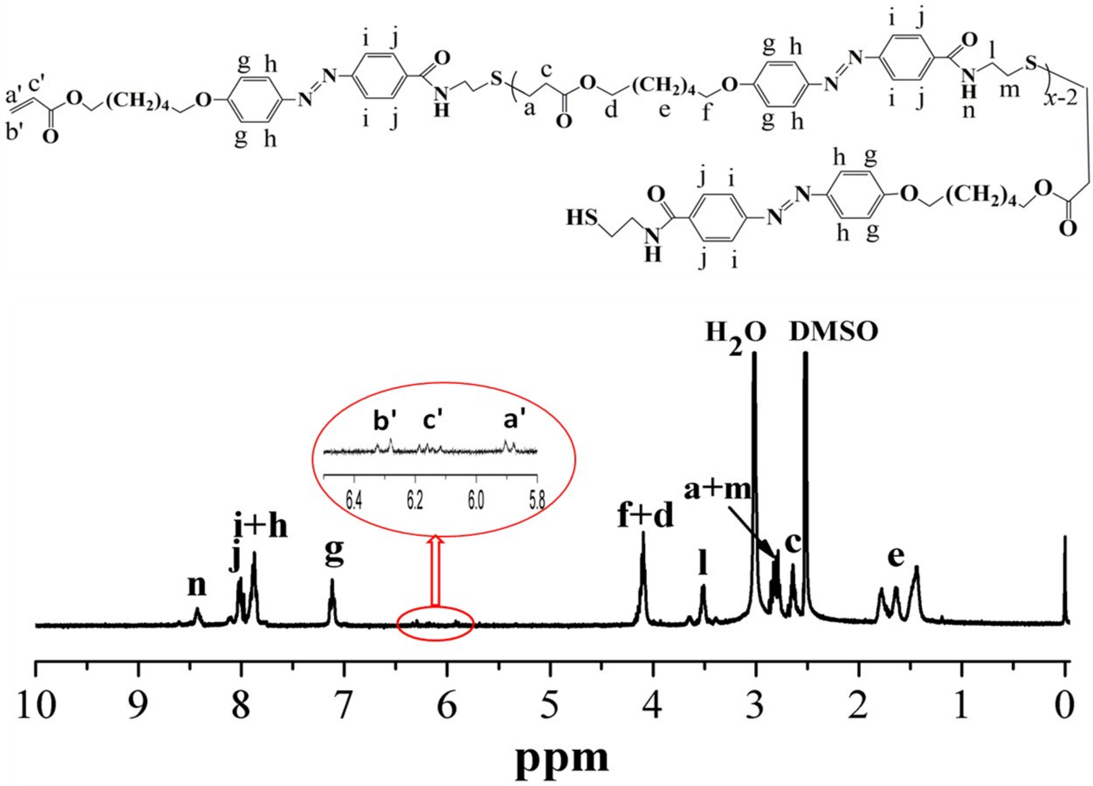


Fig. S3 The complete chemical structure of Azo-PEA-6 and its ^{1}H NMR spectrum determined in DMSO-d6 at 80 ^{o}C.

Fig. S3 presents the complete chemical structure of Azo-PEA-6 and its ^{1}H NMR spectrum (determined in DMSO-d6 at 80 ^{o}C), from which the number-average molecular weight ($M_{\mathrm{n,NMR}}$) of Azo-PEA-6 was derived to be 7580 by using the following equation (Table 1):

$$M_{\mathrm{n,NMR}} = x \times M_{\mathrm{repeat\ unit}} = [(S_{\mathrm{g}}/S_{\mathrm{a'}})/2] \times M_{\mathrm{repeat\ unit}}$$

where x refers to the number of the repeat unit in Azo-PEA-6, $M_{\mathrm{repeat\ unit}}$ is the molar mass of the repeat unit of Azo-PEA-6 (which is 455), and $S_{\mathrm{a'}}$ and S_{g} refer to the integral of the peak between 5.86-5.92 ppm (for the proton a′ in the terminal acrylate group) and that of the peak at 7.10 ppm (for the protons g in the aromatic rings), respectively.

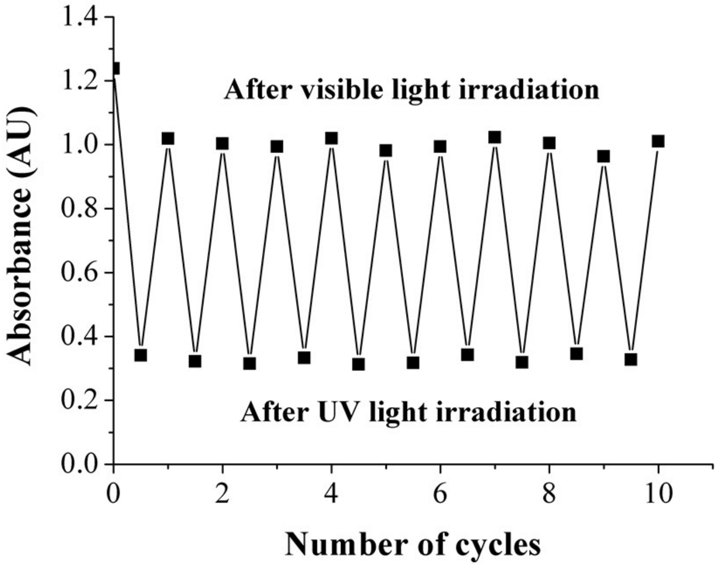


Fig. S4 UV and visible light-induced photoisomerization cycles of the Azo-PEA-6 solution in DMF (C = 50 μM repeat unit of Azo-PEA-6) at 25 °C. In each cycle, the polymer solution was first irradiated with UV light for 200 s and then with visible light for 900 s, respectively.

The fabrication of the Azo-PEA-6 film and study on its photoresponsive properties

A polymer film was cast from a solution of Azo-PEA-6 in hexafluoroisopropanol (HFIP) (1.0 mg/mL, 40 μL) on a quartz glass plate (12 × 45 mm). After the solvent was evaporated slowly at ambient temperature for 12 h, a transparent light yellow film was formed on the quartz glass plate. The thickness (l) of the polymer film is estimated to be 74 nm by using the equation $l = VC/\rho S$, where V is the volume of the polymer solution cast on the quartz glass plate, C the concentration of the polymer solution, ρ the density of the soild polymer film (ρ is assumed to be 1 g/mL here), and S the surface area of the quartz glass plate.

The photochemical isomerization of the Azo-PEA-6 film was then studied (Fig. S5). The UV-vis spectrum of the polymer film displayed one strong π-π* transition band around 345 nm (this transition band showed a large blue-shift in comparison with that of the Azo-PEA-6 solution (Fig. 3), suggesting the formation of H-aggregation among azo mesogens in the solid film), whereas no noticeable peak around 450 nm (n-π* transition band) was observed (Fig. S5a). Irradiating the polymer film with 365 nm light resulted in *trans* to *cis* photoisomerization and a photostationary state was eventually reached in about 210 s. In addition, *cis* to *trans* back-isomerization was found to take place upon irradiating the above film with $\lambda > 430$ nm light (Fig. S5b). The finally recovered absorbance of *trans*-azo isomer was lower than that before UV irradiation in this case, similar with that of the polymer solution (Fig. 3b). Furthermore, the photochemical isomerization of the polymer film also proved to be reversible upon the alternating UV and visible light irradiation (Fig. S5c).

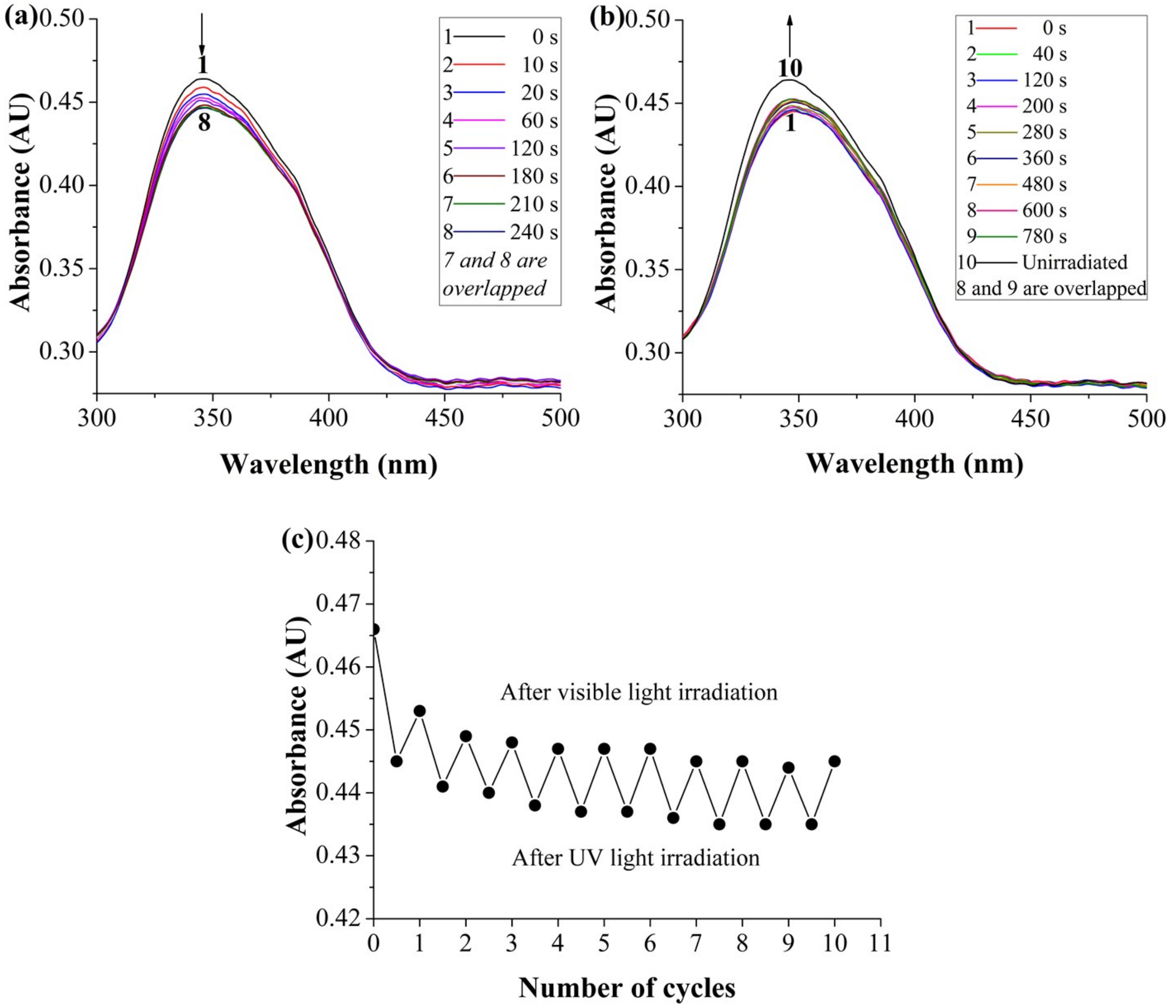
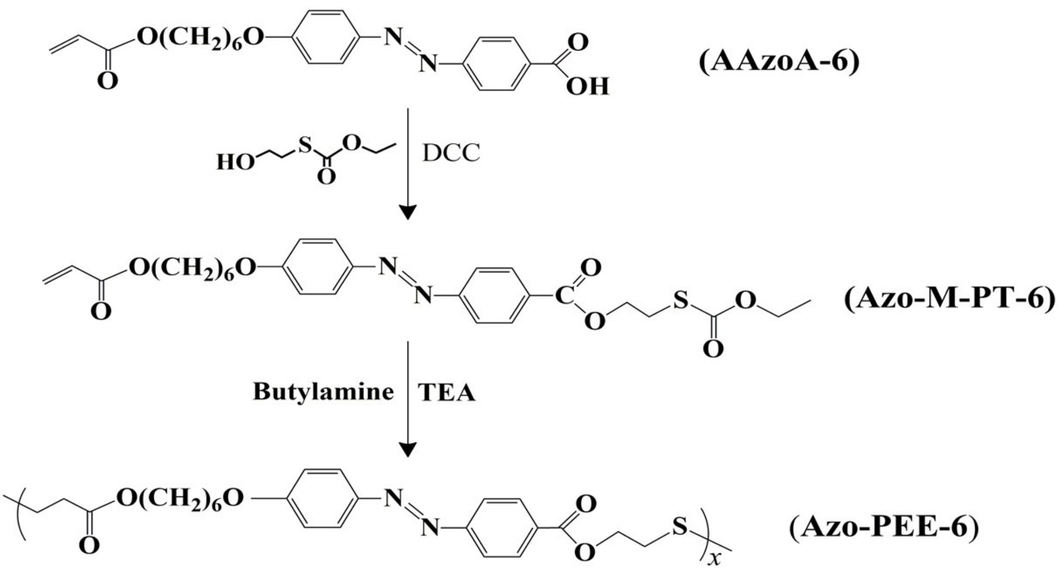


Fig. S5 (a,b) UV-vis spectral changes in dependence of time for the Azo-PEA-6 film at 25 °C upon irradiation with 365 nm light (a) and upon irradiating the film at the photostationary state with $\lambda > 430$ nm visible light (b); (c) UV and visible light-induced photoisomerization cycles of the Azo-PEA-6 film at 25 °C. In each cycle, the polymer film was first irradiated with UV light for 210 s and then with visible light for 600 s, respectively.

Synthesis of Azo-PEE-6

Azo-PEE-6 was prepared via the Michael addition polymerization of an acrylate-type azo monomer with a protected thiol group (i.e., Azo-M-PT-6) in the presence of *n*-butylamine and TEA in dried chloroform ($CHCl_3$). The synthetic route and chemical structures of Azo-M-PT-6 and Azo-PEE-6 are shown in Scheme S1.



Scheme S1 Synthetic route and chemical structures of Azo-M-PT-6 and Azo-PEE-6.

Synthesis of S-(2-hydroxylethyl)-O-ethyl dithiocarbonate. *S*-(2-Hydroxylethyl)-*O*-ethyl dithiocarbonate was synthesized following a literature procedure (Nicolaÿ, R. *Macromolecules* **2012**, *45*, 821-827): Potassium ethyl xanthogenate (10.77 g, 67.186 mmol) was first dissolved in acetone (42 mL). To this solution was added dropwise a solution of 2-bromoethanol (6.96 g, 55.693 mmol) in acetone (18 mL). After being magnetically stirred at ambient temperature for 12 h, the reaction mixture was filtered and the filtrate was evaporated to remove the solvent. The obtained solid was dissolved in $CHCl_3$ (100 mL) and the resulting solution was washed with deionized water and an aqueous solution of sodium chloride (10 wt%), dried with anhydrous magnesium sulphate overnight, and then evaporated to dryness to afford a yellow liquid (yield: 93%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.69-4.60 (q, 2H, $-(C{=}S)OCH_2-$), 3.90-3.84 (t, 2H, $HOC\underline{H_2}-$), 3.38-3.31 (t, 2H, $-(C{=}S)SCH_2-$), 1.46-1.38 (t, 3H, $-CH_3$).

Synthesis of Azo-M-PT-6. AAzoA-6 (2.00 g, 5.05 mmol), *S*-(2-hydroxylethyl)-*O*-ethyl dithiocarbonate (1.02 g, 6.14 mmol), and 4-(dimethylamino)pyridine (0.062 g, 0.51 mmol) were dissolved in dried dichloromethane (CH_2Cl_2) (40 mL) and the solution was cooled down to 0 °C. To this mixture was added dropwise a solution of *N,N'*-dicyclohexylcarbodiimide (1.05 g, 5.10 mmol) in dried CH_2Cl_2 (20 mL) under stirring. After being magnetically stirred at 0 ^oC for 1 h and at 25 ^oC for 24 h, the reaction mixture was filtered and the filtrate was evaporated to dryness. The resulting crude product was purified with silica gel column chromatography by using a mixture of petroleum ether, CH$_2$Cl$_2$, and ethyl acetate (10:1:0.1 v/v) as the eluent to provide an orange-yellow product (yield: 50%). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 8.20-8.14 (d, 2H, Ar-H), 7.99-7.85 (dd, 4H, Ar-H), 7.04-6.98 (d, 2H, Ar-H), 6.43-6.38 (d, 1H, CH=C-COO-), 6.17-6.06 (q, 1H, C=CH-COO-), 5.84-5.78 (d, 1H, CH=C-COO-), 4.70-4.61 (q, 2H, -(C=S)OCH$_2$-), 4.61-4.55 (t, 2H, -ArCOOCH$_2$-), 4.21-4.14 (t, 2H, -CH$_2$OAr-), 4.09-4.01 (t, 2H, C=C-COOCH$_2$-), 3.59-3.52 (t, 2H, -(C=S)SCH$_2$-), 1.91-1.39 (t, 11H, -(CH2)$_4$- ,-CH$_3$).

Synthesis of Azo-PEE-6. To a one-neck round-bottom flask (25 mL) with a magnetic stir bar inside was added Azo-M-PT-6 (299.8 mg, 0.552 mmol) and dried CHCl$_3$ (9.0 mL). After the above solution was bubbled with argon for 10 min, *n*-butylamine (54 µL, 0.552 mmol) was added and the mixed solution was magnetically stirred at 25 ^{o}C for 30 min. Afterwards, TEA (234 µL, 1.656 mmol) was added into the solution dropwise under the argon bubbling. The sealed reaction mixture was magnetically stirred at 40 ^{o}C for 48 h, cooled down to the room temperature, and then poured into anhydrous ethyl ether. The precipitate was collected by filtration and washed thoroughly with ethyl ether. Finally, the product was dried at 40 °C under vacuum to provide the orange-yellow Azo-PEE-6 (yield: 82%).

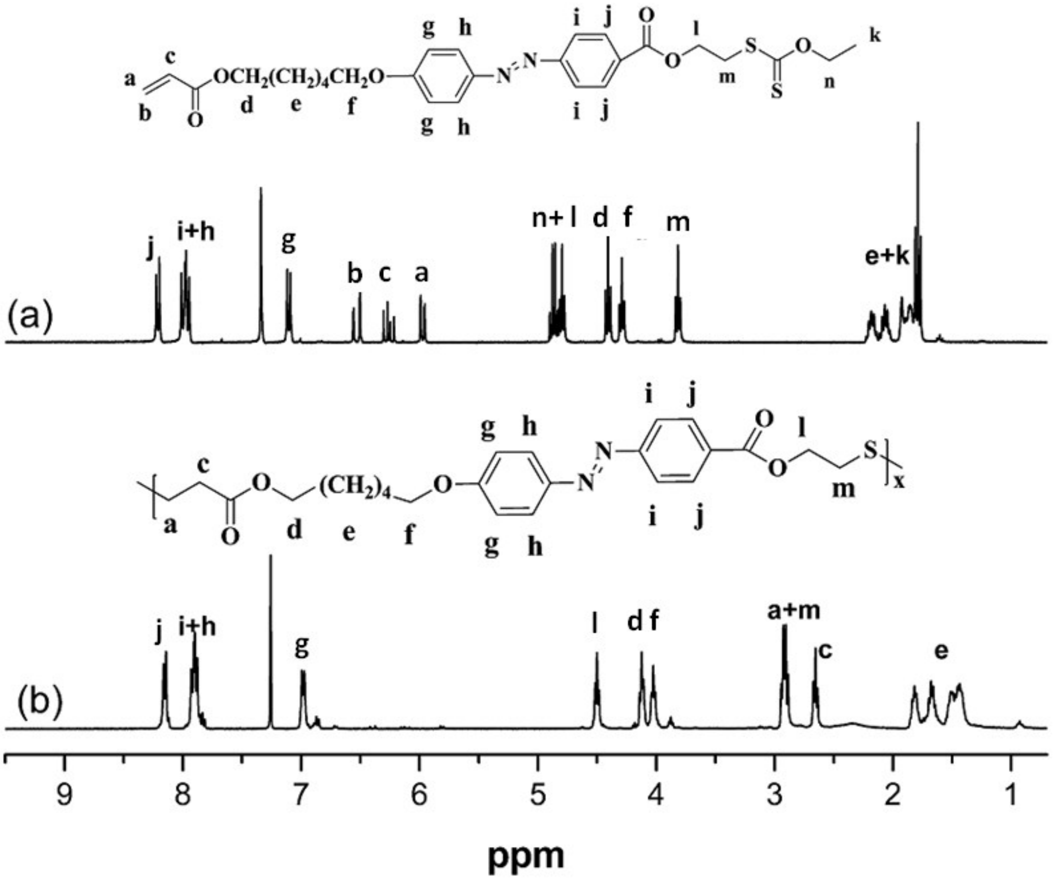


Fig. S6 ^{1}H NMR spectra of Azo-M-PT-6 (a) and Azo-PEE-6 (b) in CDCl$_3$.

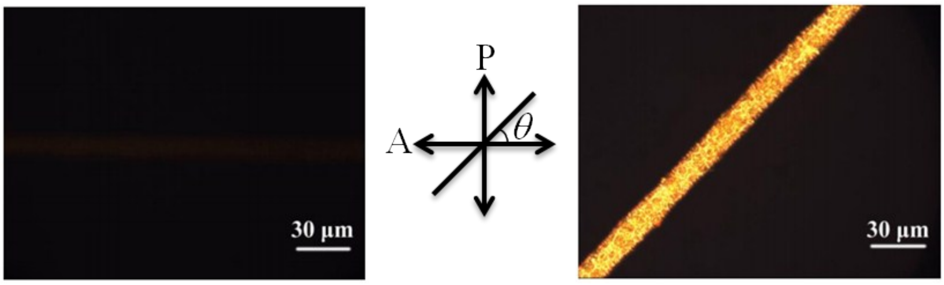


Fig. S7 POM images of the textures of an Azo-PEE-6 fiber taken at the room temperature. Sample angle to the analyzer: $\theta = 0°$ (left); $\theta = 45°$ (right).

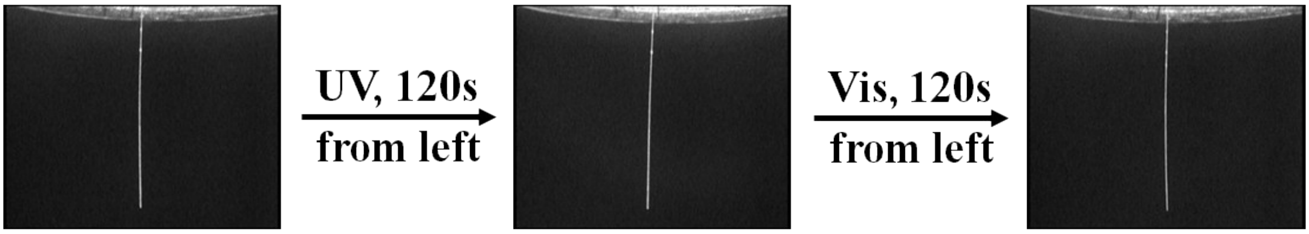


Fig. S8 Photographs of an Azo-PEE-6 fiber upon irradiation with 365 nm UV light (150 mW cm^{-2}) and visible light ($\lambda > 510$ nm, 120 mW cm^{-2}) at 90 °C. The size of the fiber is 9 mm × 21 µm.

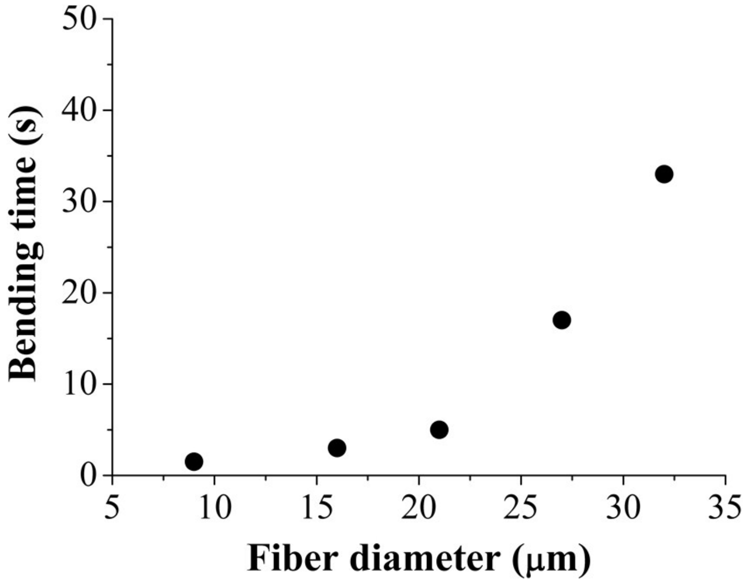


Fig. S9 Effect of the diameter of Azo-PEA-6 fibers on their bending time upon their exposure to 365 nm UV light (150 mW cm^{-2}). The length of the fiber is 9 mm.

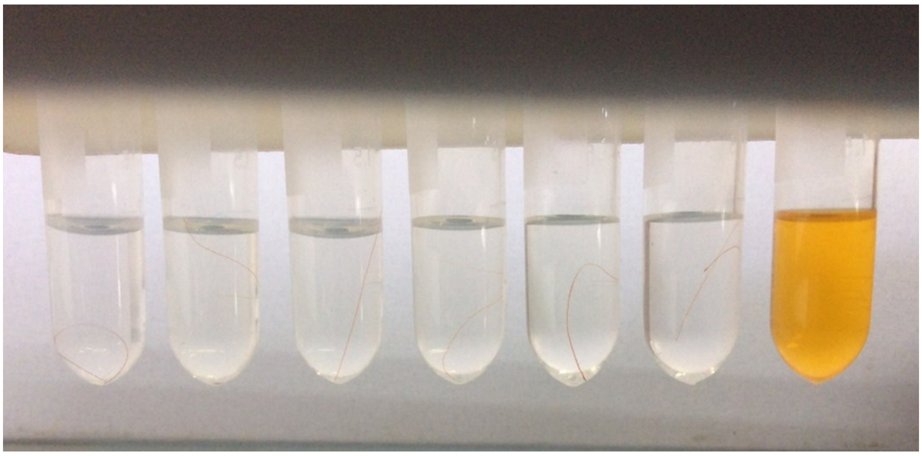


Fig. S10 Photograph of the dispersed Azo-PEA-6 fiber in different solvents (the dispersion temperature is 28 °C and dispersion time is 24 h). The solvents from left to right in the above photograph are methanol, $CHCl_3$, THF, DMF, DMSO, DMAC, and HFIP.