

## Supplementary material

### Azophenol-based liquid-crystalline elastomers for stable light-driven actuators

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## Materials and general instrumentation

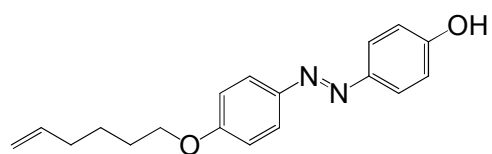
All reagents for synthesis were used as received without further purification. Flash chromatography was carried out over silica gel (SDS, 230-240 mesh). Anhydrous THF (Sharlau) was dried from sodium/benzophenone and freshly distilled before used. Commercially available anhydrous DMF (Fluka) was stored over activated 4Å molecular sieves under inert atmosphere. Melting points of the azo-monomers were determined by polarized optical microscopy (POM) using a Nikon Eclipse polarizing microscope equipped with a Linkam THMS 600 hot stage and a Linkam CI 93 programmable temperature controller at a scan rate of 5 °C min<sup>-1</sup>. FT-IR spectra were registered in a Nicolet 6700 FT-IR spectrophotometer from Thermo Scientific. Electronic spectra were recorded in a Varian Cary 500E UV-Vis-NIR spectrophotometer. <sup>1</sup>H NMR (300 MHz) and <sup>13</sup>C NMR (75 MHz) spectra were collected on a Varian Inova spectrophotometer using CDCl<sub>3</sub> as solvent. NMR spectra have been processed with the MestRec commercially available software. HRMS was performed in a LC/MSD-TOF Agilent Technologies apparatus by means of the electrospray (ESI-MS) technique. Electronic spectra were recorded in a Varian Cary 500E UV-Vis-NIR spectrophotometer.

## Synthesis of the azocompounds

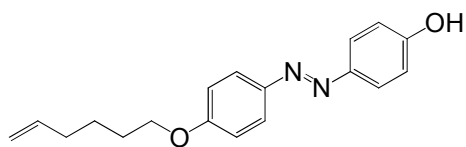
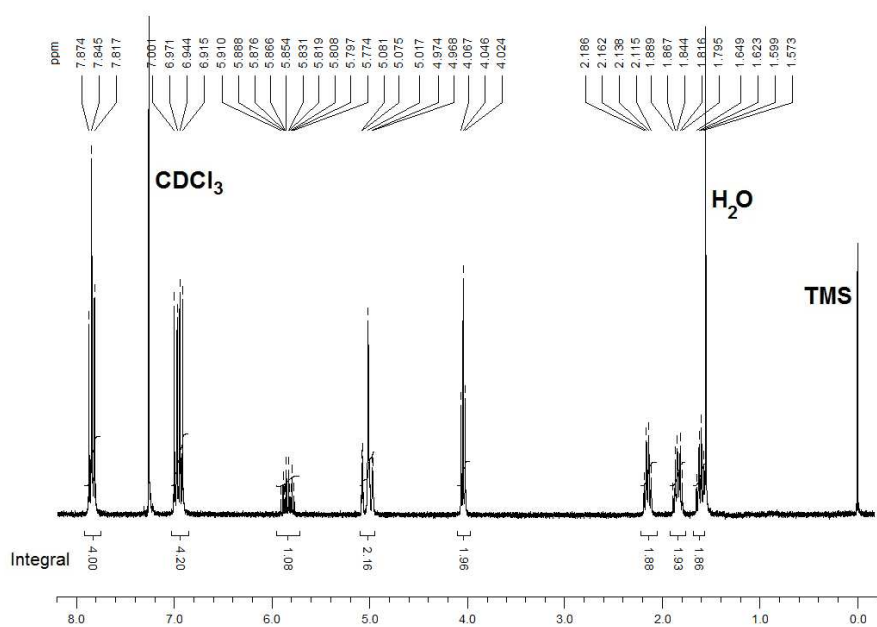
**4-(5-hexenyloxy)-4'-hydroxyazobenzene (AZO-OH).** NaH (974 mg, 60 % dispersion in mineral oil) was suspended at 0 °C in anhydrous DMF (55 cm<sup>3</sup>) under inert atmosphere. After, ethanethiol (1.8 cm<sup>3</sup>) was slowly dropped to the suspension and after the addition was finished, the resulting solution was stirred at 0 °C until the bubbling ceased (*ca.* 30 min.). Next, a solution of 4-(5-hexenyloxy)-4'-methoxyazobenzene (1.5 g) in anhydrous DMF (15 cm<sup>3</sup>) was added via cannula. The reaction mixture was heated up to 125 °C and stirred at this temperature for 3 hours. When the reaction was finished, it was cooled down, diluted with water (50 cm<sup>3</sup>) and acidified until pH = 2. The product was extracted with ethyl acetate (4 × 50 cm<sup>3</sup>) and the solvent was removed. The crude was purified by flash column chromatography using a mixture of CH<sub>2</sub>Cl<sub>2</sub> and ethyl acetate (7:3 v/v) as eluent. **AZO-OH** was obtained as an orange crystalline solid (Yield = 84 %). **m.p.** (POM): 87-88 °C. **IR** (ATR)  $\nu$  3169, 3070, 2932, 2864, 1904, 1826, 1587, 1469, 1383, 1307, 1241, 1141, 1103.1033, 999, 909, 835, 762, 726, 632 cm<sup>-1</sup>. **UV-vis** (acetonitrile):  $\lambda_{max}$  = 357 nm ( $\epsilon$  = 12 900 M<sup>-1</sup> cm<sup>-1</sup>). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 300 MHz):  $\delta$

1.61 (2H, m), 1.85 (2H, m), 2.15 (2H, m), 4.05 (2H, t,  $J = 6.3$  Hz), 5.03 (2H, m), 5.85 (1H, m), 6.93 (2H, d,  $J = 8.7$  Hz), 6.99 (2H, d,  $J = 9.0$  Hz), 7.83 (2H, d,  $J = 8.4$  Hz), 7.86 (2H, d,  $J = 8.7$  Hz) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  25.2, 28.6, 33.4, 68.1, 114.7, 114.8, 115.8, 124.3, 124.5, 138.4, 146.8, 147.0, 157.9, 161.2 ppm. HRMS (ESI-MS):  $m/z$  calcd. for  $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_2$   $[\text{MH}^+]$  297.1603; found 297.1595  $[\text{MH}^+]$ .

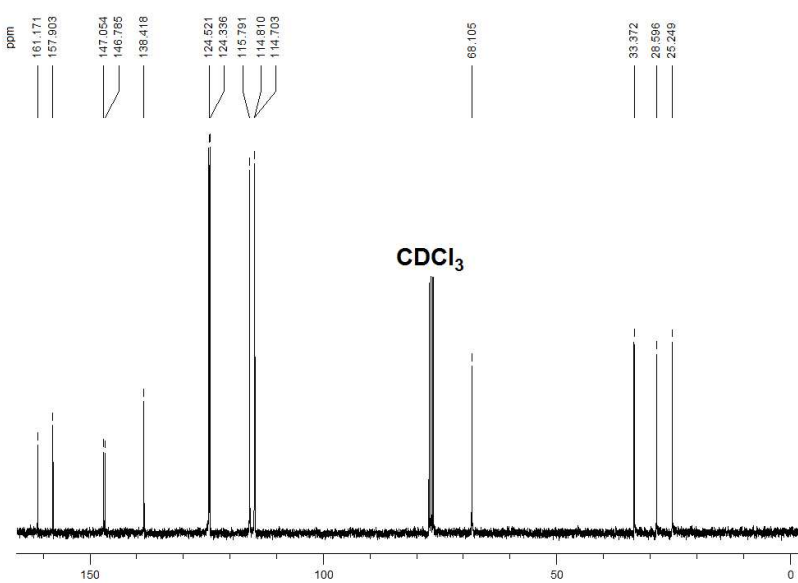
**4-acetyl-4'-(5-hexenyloxy)azobenzene (AZO-Ac).** AZO-OH (1 g) was dissolved in anhydrous THF (40  $\text{cm}^3$ ) under nitrogen atmosphere. Next, triethylamine (0.5  $\text{cm}^3$ ) and acetyl chloride (0.5  $\text{cm}^3$ ) were added. The reaction mixture was stirred at room temperature for 6 hours. Afterwards, the solvent was removed under reduced pressure. The crude was purified by flash column chromatography using a mixture of  $\text{CH}_2\text{Cl}_2$  and hexanes (3:2 v/v) as eluent. AZO-Ac was obtained as a yellow crystalline solid (Yield = 72 %). m.p. (POM): 99-100  $^\circ\text{C}$ . IR (ATR)  $\nu$  3068, 2975, 2937, 2861, 1907, 1821, 1760, 1641, 1591, 1493, 1463, 1430, 1368, 1298, 1251, 1191, 1141, 1103, 1007, 956, 909, 838, 772, 598  $\text{cm}^{-1}$ . UV-vis (toluene):  $\lambda_{\text{max}} = 350$  nm ( $\varepsilon = 20\,050$   $\text{M}^{-1}\text{cm}^{-1}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.60 (2H, m), 1.86 (2H, m), 2.15 (2H, m), 2.33 (3H, s), 4.05 (2H, t,  $J = 6.4$  Hz), 5.03 (2H, m), 5.85 (1H, m), 7.00 (2H, d,  $J = 9.0$  Hz), 7.23 (2H, d,  $J = 8.9$  Hz), 7.89 (2H, d,  $J = 9.0$  Hz), 7.91 (2H, d,  $J = 8.9$  Hz) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  21.1, 25.3, 28.6, 33.4, 68.1, 114.7, 114.8, 122.1, 123.6, 124.7, 138.4, 146.8, 150.4, 152.1, 161.7, 169.1 ppm. HRMS (ESI-MS):  $m/z$  calcd. for  $\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}_3$   $[\text{MH}^+]$  339.1709; found 339.1700  $[\text{MH}^+]$ .

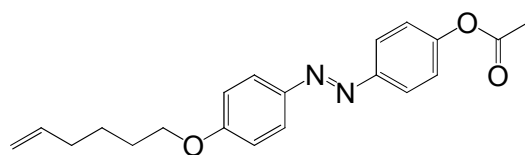


AZO-OH

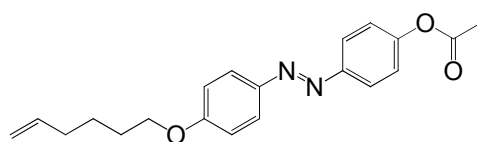
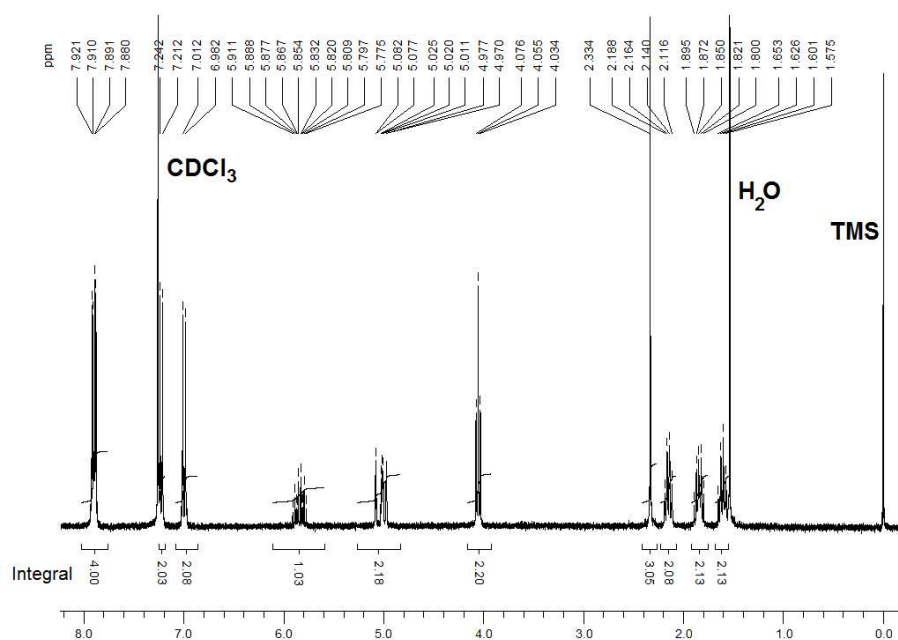


AZO-OH

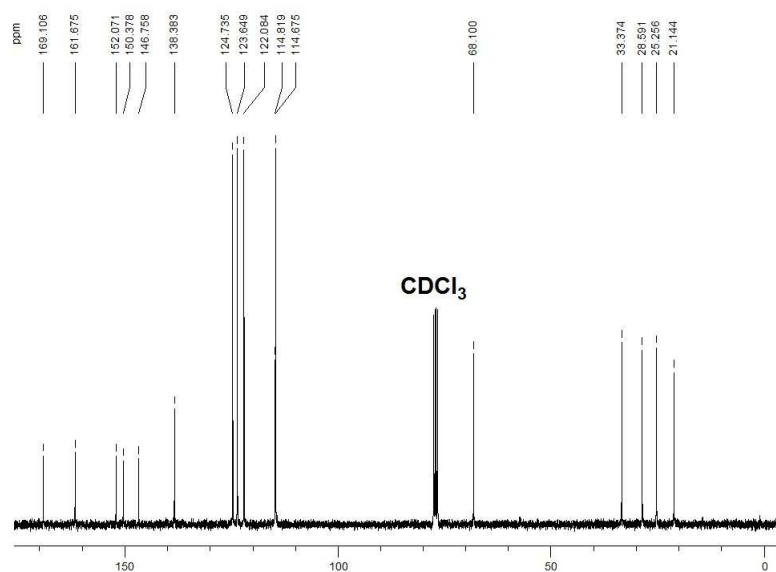




**AZO-Ac**

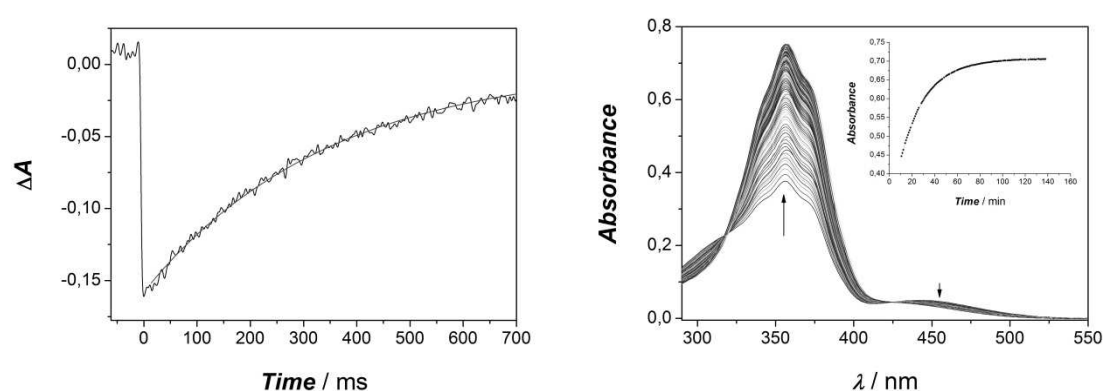


**AZO-Ac**



## Kinetic experiments

A population of *cis*-azobenzenes was generated by UV photolysis and its relaxation was followed by time-resolved UV-Vis spectroscopy. For long-lived *cis*-azobenzenes, the samples were irradiated with a Philips high-pressure mercury lamp (total nominal power 500 W) filtered with a 0.5 M solution of  $\text{Co}(\text{NO}_3)_2$  in water. Irradiation was pursued until no further changes could be observed in the electronic spectrum of the sample; the usual irradiation time was 10 minutes. Afterwards, the solutions were thermostated in the dark at the desired temperature ( $\pm 0.1$  K) and the thermal *cis*-to-*trans* isomerisation was monitored by absorption spectroscopy using a Varian Cary 500E UV-Vis-NIR spectrophotometer. For short-lived samples, the thermal *cis*-to-*trans* isomerisation process was studied by means of laser flash-photolysis. Thus, the *cis* isomer of the corresponding azoderivative was generated by a Q-switched Nd-YAG laser (355 nm, 5 ns pulse width, 1-10 mJ per pulse) and the time evolution of the sample absorbance was monitored at 90 degrees by a white-light beam produced by a PTI 75 W Xe lamp. The light transmitted by the sample was spectrally resolved using a monochromator and detected with a Hamamatsu R928 photomultiplier, whose output was fed into a digital oscilloscope through a 50 Ohm resistor. The observation wavelength was set at 370 nm in all the cases. No isomerisation of the azocompounds was promoted by observation wavelength of the spectrophotometer. The experiments were realized in 1 cm optical path quartz cells (Hellma). No photo-degradation of the compounds was observed.



**Figure S2.** Transient generated by laser pulse irradiation with UV-light ( $\lambda = 355$  nm) for AZO-OH in ethanol (left) and changes in the electronic spectrum of an AZO-OH *cis*-to-*trans* isomerising toluene solution at 298 K (right,  $\Delta t = 48$  s, [AZO-OH] = 0.02 mM).

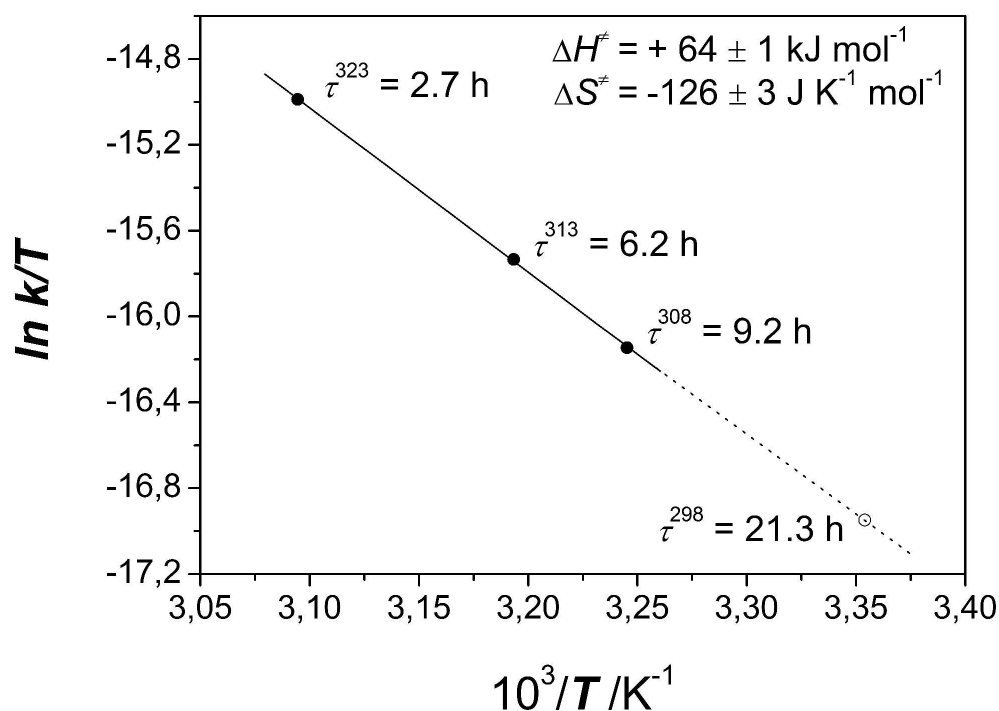
## **Characterization of the liquid-crystalline behavior of the LSCEs**

The characterization of the liquid-crystalline behavior of the networks was carried out by using the standard techniques: X-Ray scattering, differential scanning calorimetry and swelling and thermo-mechanical experiments. DSC measurements were performed in a Perkin Elmer DSC-7 apparatus under nitrogen atmosphere at heating rates of 9, 16, 25 and 36 K min<sup>-1</sup>. The transformation temperatures were determined by extrapolating to a heating rate of 0 K min<sup>-1</sup>. XRD measurements were carried out with the monochromatic Cu K $\alpha$  radiation ( $\lambda=1.5418\text{\AA}$ ), using a two-dimensional image plate system as detector. The incident beam was normal to the surface of the elastomer. XRD experiments were realized at room temperature. The effective cross-linking density was analyzed by means of swelling experiments. The dimensions of the network in the deswollen and swollen state in toluene were measured at room temperature with a Will Strübin-Wetzlar optical microscope. Thermo-mechanical experiments were performed in a homemade apparatus developed by P. Fischer. The sample was introduced in a triple wall glass column. The dimensions of the network in the direction of the strain axis were measured in the cooling process of the network from the isotropic state in the temperature range from 288 to 373 K. The temperature was controlled by a thermostat and the silicon oil of the outer circuit flowed through the inner spacing of the column whereas the outer spacing was evacuated to obtain thermal insulation. The temperature inside the glass column was controlled by means of a Pt100 thermoresistor. A PC logged the series of required temperatures and took digitalized images of the sample each 2 K by means of a video camera and a frame grabber card after a period of 30 min. The digitalized images were analyzed by digital imaging processing after the experiment.

## **Opto-mechanical measurements**

Opto-mechanical experiments were performed in a self-constructed apparatus designed to measure the retractive force generated in the network as a function of time under irradiation with light of the appropriate wavelength or in the thermal relaxation process in the dark. It should be highlighted that the setup design allowed the minimization of all thermal effects. The rectangular samples (9 mm  $\times$  1 mm  $\times$  300-400  $\mu\text{m}$ ) were pasted within two metallic rigid clamps and fixed inside the measurement cell. The cell was thermostated at the corresponding temperature during all the measurement. The

temperature of the cell was controlled by a Julabo MB thermostat. Before starting the measurement, the samples were equilibrated at the corresponding temperature for 1 hour. After that, the samples were stretched to a residual stress value between 21 and 23 kPa with an Owis SM400 microstep motor. The samples were left to reach equilibrium at this small extension. Once the residual stress value was constant with time, the samples were then irradiated with UV light of  $\lambda = 380$  nm. The light source was an Osram XBO150W/1 xenon arc lamp (150 W, 20 V, 7.5 A). The wavelength selection was done with a Jobin Yvon H20 UV/Vis/NIR monochromator. The wavelength of the incident light was controlled with an Ocean Optics USB2000 UV-Vis spectrophotometer (UV2/OFLV-4 detector, L2 lens, 5  $\mu\text{m}$  slit, 200-850 nm) which was placed in the back side of the measurement cell through an optical fiber (UV/Vis, 2 m, 400  $\mu\text{m}$ ). The stress generated in the sample by the light was measured by a Transducer Techniques GS0-10 transducer load cell (10 g) and analyzed by a Newport Electronics INFS-1001-DC7 high performance strain gage indicator. All the parameters, such as time, light wavelength, temperature of the cell and sample stress were continuously logged and controlled by means of a PC containing the LabView 7.5 software (National Instruments).



**Figure S3.** Eyring plot for the thermal *cis*-to-*trans* isomerization of the LSCE EAZO-Ac.