Supporting Information

Opto-mechanical Effect in Photoactive Nematic Side-Chain Liquid-Crystalline Elastomers

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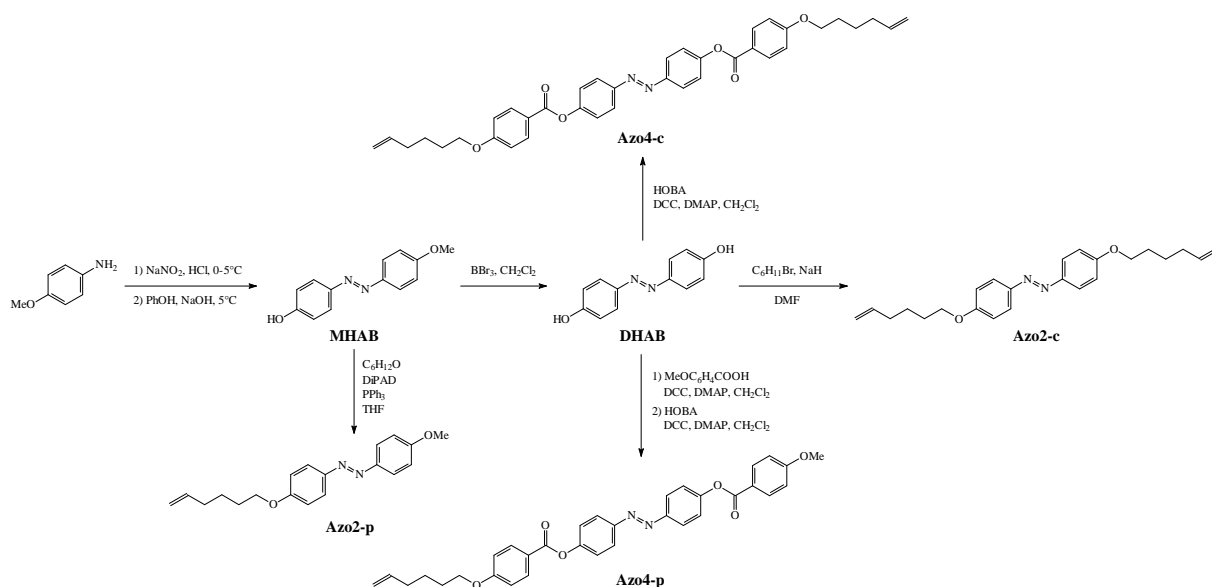Fax: +41 44 632 1603; E-mail: antoni.sanchez@agrl.ethz.ch

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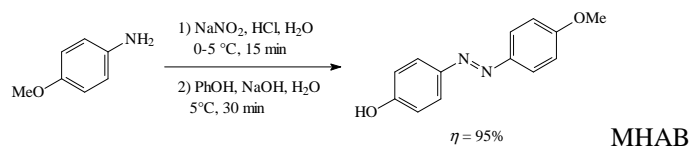
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Scheme SI-1. Synthetic route for the four azoderivatives: Azo2-p, Azo2-c, Azo4-p and Azo4-c.
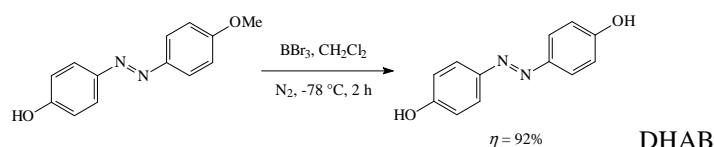
Synthesis of (E)-4-hydroxy-4'-methoxyzobenzene (MHAB)

In a 50 mL round-bottomed flask, 1.0 g (8 mmol) of 4-methoxyaniline was placed, and 10 mL of water and 5 mL of 37% HCl solution and some crushed ice were added. This solution was cooled at 0 °C with an external ice-water bath. Then 616 mg (9 mmol) of $NaNO_2$ in 5 mL of water were added at 0-5 °C, and leaving the formation of 4-methoxybenzenediazonium chloride during 15 min. In next step, in a 100 mL flask, 764 mg (8 mmol) of phenol and 2.7 g of NaOH were placed, and 10 mL of water were added. This other solution was kept below 5 °C. Afterwards, the first solution of the diazonium salt was dropped slowly, being observed the appearance of a red color compound. After 30 min the azobenzene derivative was precipitated using 2 M HCl solution. The precipitate was filtered, washed several times with water, dried and chromatographed in a silica gel column (CH_2Cl_2). Yield: 1.8 g (95%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (2H, d, o-Ar, J=9.5 Hz), 7.82 (2H, d, m-Ar', J=8.8 Hz), 7.00 (2H, d, m-Ar', J=8.8 Hz), 6.92 (2H, d, o-Ar, J=9.5 Hz), 5.44 (1H, s, ArOH), 3.89 (3H, s, CH_3O) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.5 (Ar'OCH_3), 157.6 (ArOH), 147.1 (Ar'N=N), 146.9 (ArN=N), 124.5 (o-ArH), 124.3 (o-Ar'H), 115.7 (m-ArH), 114.1 (m-Ar'H), 55.6 (CH_3O) ppm. FTIR (NaCl): 3625 (st, O-H), 1495 (st, N=N), 1238 (st, C-O) cm^{-1}. m.p.: 142 °C
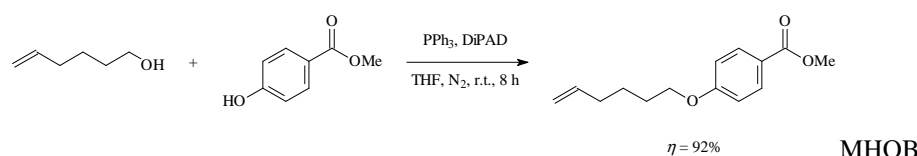
Synthesis of (E)-4,4'-dihydroxyazobenzene (DHAB)

In a 100 mL round-bottomed flask, 1.0 g (4 mmol) of (E)-4-hydroxy-4'-methoxyzobenzene (MHAB) were placed under nitrogen at –78 °C, and 17.5 mL of 1 M BBr_3 solution in CH_2Cl_2 were added slowly. After the addition the mixture was warming up at room temperature and controlled by TLC (SiO_2, AcOEt/hexane, 1:1). After 2h the mixture was cooled at 0 °C, and 2 M NaOH solution was added. Then 2 M HCl was added until pH = 1, and extracted with AcOEt. The solution was filtered and evaporated. The residue was chromatographed in a silica gel column (AcOEt/hexane, 1:1 v/v). Yield: 0.9 g (92%).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 10.10 (2H, s, ArOH), 7.71 (4H, d, o-Ar, J=8.8 Hz), 6.90 (4H, d, m-Ar, J=8.6 Hz) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ = 160.1 (2C, ArOH), 145.6 (2C, ArN=N), 124.3 (4C, o-ArH), 115.9 (4C, m-ArH) ppm. FTIR (NaCl): 3598 (st, O-H), 1492 (st, N=N) cm^{-1}. m.p.: 218 °C
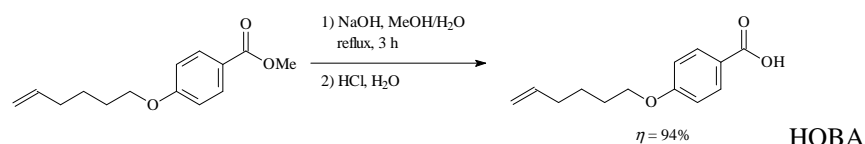
Synthesis of methyl 4-(hex-5-en-1-yloxy)benzoate (MHOB)

$\eta = 92\%$ MHOB

In a 500 mL round-bottomed flask, 25.0 g (164 mmol) of methyl 4-hydroxybenzoate, and 47.4 g (181 mmol) of triphenylphosphine (PPh_3) were placed, and 150 mL of anhydrous THF were added. The system was magnetically stirred and purged with nitrogen for 15 min. Afterwards, 16.5 g (164 mmol) of 5-hexen-1-ol were added. In next step, the solution was magnetically stirred under nitrogen, and 36.6 g (181 mmol) of diisopropyl aza-1,2-dicarboxylate (DiPAD) were added. The reaction was stirred at room temperature and controlled by TLC (SiO_2, CH_2Cl_2). It was finished, when the complete disappearance of the starting phenol derivative (8 h) was observed. Then hexane/AcOEt (5:1 v/v) was added and a white solid, triphenylphosphine oxide, was precipitated. The solution was filtered and evaporated. The residue was chromatographed in a silica gel column (CH_2Cl_2). Yield: 38.5 g (92%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (2H, d, *o*-Ar, *J*=9.0 Hz), 6.87 (2H, d, *m*-Ar, *J*=9.0 Hz), 5.81 (1H, ddt, C$\underline{H}$=CH$_2$, *J*=17.0 Hz, *J*=10.3 Hz, *J*=6.8 Hz), 5.02 (1H, ddt, *cis*-CH=C$\underline{H}_2$, *J*=17.3 Hz, *J*=1.8 Hz, *J*=1.5 Hz), 4.96 (1H, ddt, *trans*-CH=C$\underline{H}_2$, *J*=10.2 Hz, *J*=1.8 Hz, *J*=1.5 Hz), 3.97 (2H, t, CH$_2$O, *J*=6.5 Hz), 3.85 (3H, s, CH$_3$O), 2.11 (2H, dtt, CH$_2$, *J*=7.2 Hz, *J*=7.0 Hz, *J*=1.3 Hz), 1.79 (2H, tt, CH$_2$, *J*=6.8 Hz, *J*=6.3 Hz), 1.55 (2H, tt, CH$_2$, *J*=7.5 Hz, *J*=7.3 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.7 (COOAr), 162.8 (ArOCH$_2$), 138.2 ($\underline{C}$H=CH$_2$), 131.4 (2C, *o*-ArH), 122.2 (ArCOO), 114.7 (CH=$\underline{C}$H$_2$), 113.9 (2C, *m*-ArH), 67.8 (CH$_2$O), 51.6 (CH$_3$O), 33.2 (CH$_2$), 28.4 (CH$_2$), 25.1 (CH$_2$) ppm. FTIR (NaCl): 1718 (st, C=O), 1606 (st, C=CH$_2$), 1253 (st, C–O) cm^{-1}. m.p.: oil

Synthesis of 4-(hex-5-en-1-yloxy)benzoic acid (HOBA)
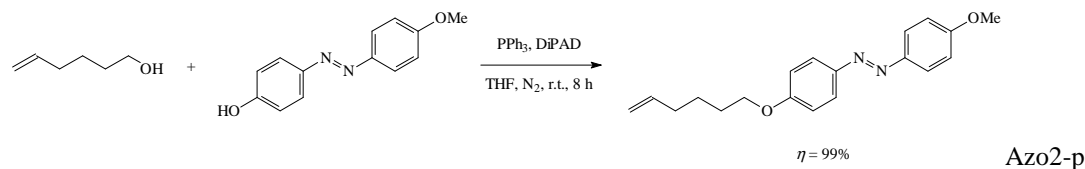

$\eta = 94\%$ HOBA

In a 500 mL round-bottomed flask, 37.0 g (158 mmol) of methyl 4-(hex-5-en-1-yloxy)benzoate (MHOB), and 15.8 g (395 mmol) of NaOH were placed, and 300 mL of (1:2 v/v) water/methanol were added. The system was magnetically stirred and brought to reflux and controlled by TLC (SiO_2, CH_2Cl_2). It was finished, when the complete disappearance of the starting ester derivative (3 h) was observed. Then, after cooling, 1M HCl solution was added and the precipitated free carboxylic acid was extracted with CH_2Cl_2. The organic solution was filtered and evaporated. The isolated white solid was recrystallized from CH_2Cl_2. Yield: 32.4 g (94%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.38 (1H, s, COOH), 8.06 (2H, d, *o*-Ar, *J*=9.0 Hz), 6.93 (2H, d, *m*-Ar, *J*=9.0 Hz), 5.83 (1H, ddt, C$\underline{H}$=CH$_2$, *J*=17.0 Hz, *J*=10.3 Hz, *J*=6.8 Hz), 5.05 (1H, ddt, *cis*-CH=C$\underline{H}_2$, *J*=17.3 Hz, *J*=1.8 Hz, *J*=1.5 Hz), 4.99 (1H, ddt, *trans*-CH=C$\underline{H}_2$, *J*=10.0 Hz, *J*=1.7 Hz, *J*=1.3 Hz), 4.03 (2H, t, CH$_2$O, *J*=6.4 Hz), 2.14 (2H, dtt, CH$_2$, *J*=7.3 Hz, *J*=6.8 Hz, *J*=1.4 Hz), 1.83 (2H, tt, CH$_2$, *J*=7.0 Hz, *J*=6.3 Hz), 1.59 (2H, tt, CH$_2$, *J*=7.5 Hz, *J*=7.0 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.2 (COOH), 163.6 (ArOCH$_2$), 138.3 ($\underline{C}$H=CH$_2$),

132.3 (2C, *o*-ArH), 121.5 (ArCOO), 114.8 (CH=$\underline{C}$H$_2$), 114.1 (2C, *m*-ArH), 68.0 (CH$_2$O), 33.3 (CH$_2$), 28.5 (CH$_2$), 25.2 (CH$_2$) ppm.
FTIR (NaCl): 3311 (st, COO–H), 1683 (st, C=O), 1606 (st, C=CH$_2$), 1257 (st, C–O) cm^{-1}. m.p. C 99 N 129 I °C
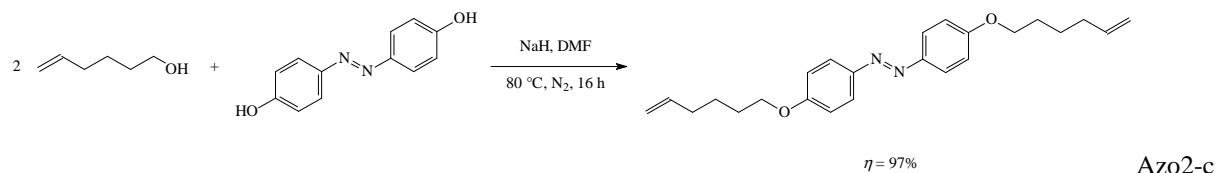
Synthesis of (E)-4-(hex-5-en-1-yloxy)-4'-methoxyazobenzene (Azo2-p)

In a 50 mL round-bottomed flask, 250 mg (1.1 mmol) of (*E*)-4-hydroxy-4'-methoxyazobenzene (MHAB), and 316 mg (1.2 mmol) of triphenylphosphine (PPh$_3$) were placed, and 15 mL of anhydrous THF were added. The system was magnetically stirred and purged with nitrogen for 15 min. Afterwards, 120 mg (0.14 mL, 1.2 mmol) of 5-hexen-1-ol were added. In next step, the solution was magnetically stirred under nitrogen, and 245 mg (1.2 mmol) of diisopropyl aza-1,2-dicarboxylate (DiPAD) were added. The reaction was stirred at room temperature and controlled by TLC (SiO$_2$, CH$_2$Cl$_2$). It was finished, when the complete disappearance of the starting phenol derivative (8 h) was observed. Then hexane/AcOEt (5:1 v/v) was added and a white solid, triphenylphosphine oxide, was precipitated. The solution was filtered and evaporated. The residue was chromatographed in a silica gel column (CH$_2$Cl$_2$/hexane, 1:1, v/v). Yield: 334 mg (99%).
^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.89 (4H, d, *o*-Ar, *J*=9.2 Hz), 7.01 (4H, d, *m*-Ar, *J*=9.2 Hz), 5.85 (1H, ddt, C$\underline{H}$=CH$_2$, J=17.1 Hz, J=10.2 Hz, J=6.7 Hz), 5.06 (1H, ddt, *cis*-CH=C$\underline{H}_2$, *J*=17.1 Hz, *J*=2.0 Hz, *J*=1.6 Hz), 5.00 (1H, ddt, *trans*-CH=C$\underline{H}_2$, *J*=10.2 Hz, *J*=2.0 Hz, *J*=1.0 Hz), 4.04 (2H, t, CH$_2$O, *J*=6.5 Hz), 3.88 (3H, s, CH$_3$O), 2.16 (2H, tdt, CH$_2$, *J*=7.1 Hz, *J*=6.7 Hz, *J*=1.2 Hz), 1.84 (2H, tt, CH$_2$, *J*=7.1 Hz, *J*=6.5 Hz), 1.60 (2H, tt, CH$_2$, *J*=7.1 Hz, *J*=5.9 Hz) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 161.0 (ArOCH$_3$), 160.6 (ArOCH$_2$), 146.6 (ArN=N), 146.4 (ArN=N), 138.0 ($\underline{C}$H=CH$_2$), 123.9 (2C, *o*-ArH), 123.5 (2C, *o*-ArH), 114.4 (CH=$\underline{C}$H$_2$), 113.8 (2C, *m*-ArH), 113.7 (2C, *m*-ArH), 114.8 (CH=$\underline{C}$H$_2$), 67.6 (CH$_2$O), 55.1 (CH$_3$O), 32.9 (CH$_2$), 28.2 (CH$_2$), 24.8 (CH$_2$) ppm. FTIR (NaCl): 1603 (st, C=CH$_2$), 1498 (st, N=N), 1250 (st, C-O), 910 (δ oop, CH=CH$_2$) cm^{-1}. UV (EtOH, 25 °C): λ_{max} = 355, 436 nm (ε = 24000, 2100 L·mol^{-1}·cm^{-1}). m.p.: C 72 N 89 I °C. C$_{19}$H$_{22}$N$_2$O$_2$ – 310.39: Calcd. C 73.52, H 7.14, N 9.03, O 10.31; Found C 73.36, H 7.16, N 9.04.

Synthesis of (E)-4,4'-bis(hex-5-en-1-yloxy)azobenzene (Azo2-c)

In a 50 mL two-necked round-bottomed flask, 200 mg (0.093 mmol) of (*E*)-4,4'-dihydroxyazobenzene (DHAB) and 7.8 mg (0.20 mmol) of NaH (60% dispersion in mineral oil) were weighted. Then a reflux condenser was attached and the system was purged with nitrogen for about 20 min, after which 10 mL of anhydrous DMF were added. The solution was magnetically stirred and heated to 80 °C; 30 mg (0.19 mmol) of 6-bromo-1-hexen dissolved in 2 mL anhydrous DMF were added. After 16 h the reaction was cooled to room

temperature and diluted with 50 mL of CH_2Cl_2 and 50 mL of H_2O and extracted with CH_2Cl_2. The organic layer was dried over anhydrous sodium sulphate, filtered and evaporated. The crude product was purified by silica gel chromatography (CH_2Cl_2/hexane, 4:6 v/v). Yield: 340 mg (97%).

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.87 (4H, d, *o*-Ar, *J*=9.0 Hz), 6.99 (4H, d, *m*-Ar, *J*=9.0 Hz), 5.85 (2H, ddt, C<u>H</u>=CH$_2$, *J*=16.9 Hz, *J*=10.4 Hz, *J*=6.7 Hz), 5.06 (2H, ddt, *cis*-CH=C<u>H</u>$_2$, *J*=17.3 Hz, *J*=2.0 Hz, *J*=1.6 Hz), 5.00 (2H, ddt, *trans*-CH=C<u>H</u>$_2$, *J*=10.2 Hz, *J*=2.0 Hz, *J*=1.0 Hz), 4.04 (4H, t, CH$_2$O, *J*=6.3 Hz), 2.15 (4H, tdt, CH$_2$, *J*=7.3 Hz, *J*=6.9 Hz, *J*=1.2 Hz), 1.84 (4H, tt, CH$_2$, *J*=6.9 Hz, *J*=6.5 Hz) 1.60 (4H, tt, CH$_2$, *J*=7.1 Hz, *J*=6.7 Hz) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 161.1 (2C, ArOCH$_2$), 147.0 (2C, ArN=N), 138.4 (2C, <u>C</u>H=CH$_2$), 124.3 (4C, *o*-ArH), 114.8 (2C, CH=<u>C</u>H$_2$), 114.6 (4C, *m*-ArH), 68.0 (2C, CH$_2$O), 33.4 (2C, CH$_2$), 28.6 (2C, CH$_2$), 25.3 (2C, CH$_2$) ppm. FTIR (NaCl): 1603 (st, C=CH$_2$), 1498 (st, N=N), 1250 (st, C-O), 910 (δ oop, CH=CH$_2$) cm^{-1}.

UV (EtOH, 25 °C): λ_{max} = 356, 436 nm (ε = 25000, 3000 L·mol^{-1}·cm^{-1}). m.p.: C$_1$ 74 C$_2$ 97 I °C. C$_{24}$H$_{30}$N$_2$O$_2$ - 378.51**:** Calcd. C 76.16, H 7.99, N 7.40, O 8.45; Found C 76.20, H 7.96, N 7.42.

Synthesis of (E)-4-[4-(hex-5-en-1-yloxy)benzoyloxy]-4'-(4-methoxybenzoyloxy)azobenzene (Azo4-p)

Azo4-p

Step 1: synthesis of (*E*)-4-hydroxy-4'-(4-methoxybenzoyloxy)azobenzene. In a 50 mL round-bottomed flask, 259 mg (1.9 mmol) of 4-methoxybenzoic acid, 440 mg (2.1 mmol) of *N,N'*-dicyclohexylcarbodiimide (DCC) and 23 mg (0.19 mmol) of 4-dimethylaminopyridine (DMAP) were placed. After 30 min of stirring and purging with nitrogen, 10 mL of anhydrous CH_2Cl_2 were added. In another 25 mL flask 415 mg (1.9 mmol) of (*E*)-4,4'-dihydroxy-azobenzene (DHAB) were weighted and dissolved in 10 mL of anhydrous THF under nitrogen atmosphere. The last solution was then transferred by canula to the first flask. The reaction was stirred at room temperature for 5 h. The urea derivative was filtered off, and the reaction mixture was then diluted with 2 M NaOH, and extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous sodium sulphate and filtered. After evaporation of the solvent, the crude product was purified by flash chromatography (SiO$_2$, CHCl$_3$, CHCl$_3$/AcOEt, 98:2, 95:5 v/v)). Yield: 200 mg (30%).

^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.15 (2H, d, *o*-Ar, *J*=9.1 Hz), 8.00 (2H, d, *o*-Ar', *J*=8.4 Hz), 7.57 (2H, d, *m*-Ar, *J*=9.1 Hz), 7.35 (2H, d, *m*-Ar, *J*=8.8 Hz), 6.91 (2H, d, *o*-Ar, *J*=8.8 Hz), 6.86 (2H, d, *m*-Ar', *J*=8.4 Hz), 3.84 (3H, s, CH$_3$O) ppm.

Step 2: 144 mg (0.41 mmol) of (*E*)-azobenzene monoester derivative obtained in the first step, 86 mg (0.41 mmol) of *N,N'*-dicyclohexylcarbodiimide (DCC), 5 mg (0.04 mmol) of 4-dimethylaminopyridine (DMAP) and 91.2 mg (0.41 mmol) of 4-(hex-5-en-1-yloxy)benzoic acid (HOBA) were placed in a 50 mL round-bottomed flask. The system was magnetically stirred and purged with nitrogen for about 15 min, and 10 mL of anhydrous CH_2Cl_2 were added. The reaction was stirred at room temperature for 5 h, and then refluxed for 1 hour. The urea derivative was filtered off, and the reaction mixture was cooled to room temperature, diluted with 2 M NaOH, and extracted with CH_2Cl_2. The combined organic layers were dried

over anhydrous sodium sulphate and filtered. After evaporation of the solvent, the crude product was purified by chromatography on silica gel using CH_2Cl_2 as an eluting solvent. Yield: 63 mg (63%).

^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.15 (4H, d, o-Ar, J=9.1 Hz), 8.00 (4H, d, o-Ar', J=8.4 Hz), 7.39 (4H, d, m-Ar, J=8.8 Hz), 6.99 (2H, d, m-Ar', J=8.4 Hz), 6.86 (2H, d, m-Ar', J=8.4 Hz), 5.85 (1H, ddt, C$\underline{H}$=CH$_2$, J=16.9 Hz, J=10.4 Hz, J=6.7 Hz), 5.06 (1H, ddt, cis-CH=C$\underline{H}_2$, J=17.3 Hz, J=2.0 Hz, J=1.6 Hz), 5.00 (1H, ddt, $trans$-CH=C$\underline{H}_2$, J=10.2 Hz, J=2.0 Hz, J=1.0 Hz), 4.07 (2H, t, CH$_2$O, J=6.3 Hz), 3.91 (3H, s, CH$_3$O), 2.14 (2H, tdt, CH$_2$, J=7.3 Hz, J=6.9 Hz, J=1.2 Hz), 1.85 (2H, tt, CH$_2$, J=6.9 Hz, J=6.5 Hz), 1.55 (2H, tt, CH$_2$, J=7.1 Hz, J=6.7 Hz) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 164.8 (ArOCH$_3$), 164.8 (COO), 164.3 (COO), 163.9 (Ar'O), 153.4 (2C, ArOCH$_2$), 150.3 (2C, ArN=N), 138.8 ($\underline{C}$H=CH$_2$), 132.6 (4C, o-Ar'H), 124.3 (4C, o-ArH), 122.7 (4C, m-ArH), 122.5 (Ar'COO), 122.2 (Ar'COO), 115.1 (CH=$\underline{C}$H$_2$), 114.6 (2C, m-Ar'H), 114.1 (2C, m-Ar'H), 68.3 (CH$_2$O), 55.8 (CH$_3$O), 33.5 (CH$_2$), 28.7 (CH$_2$), 25.5 (CH$_2$) ppm. FTIR (NaCl): 1732 (st, C=O), 1606 (st, C=CH$_2$), 1506 (st, N=N), 1259 (st, C-O), 1171 (st, C-O), 910 (δ oop, CH=CH$_2$) cm^{-1}. UV (EtOH, 25 °C): λ_{max} = 333, 435 nm (ε = 24000, 1400 L·mol^{-1}·cm^{-1}). m.p.: C 101 SmC 127 I °C. C$_{33}$H$_{30}$N$_2$O$_6$ – 550.61: Calcd. C 71.99, H 5.49, N 5.09, O 17.43; Found C 72.02, H 5.44, N 5.10.

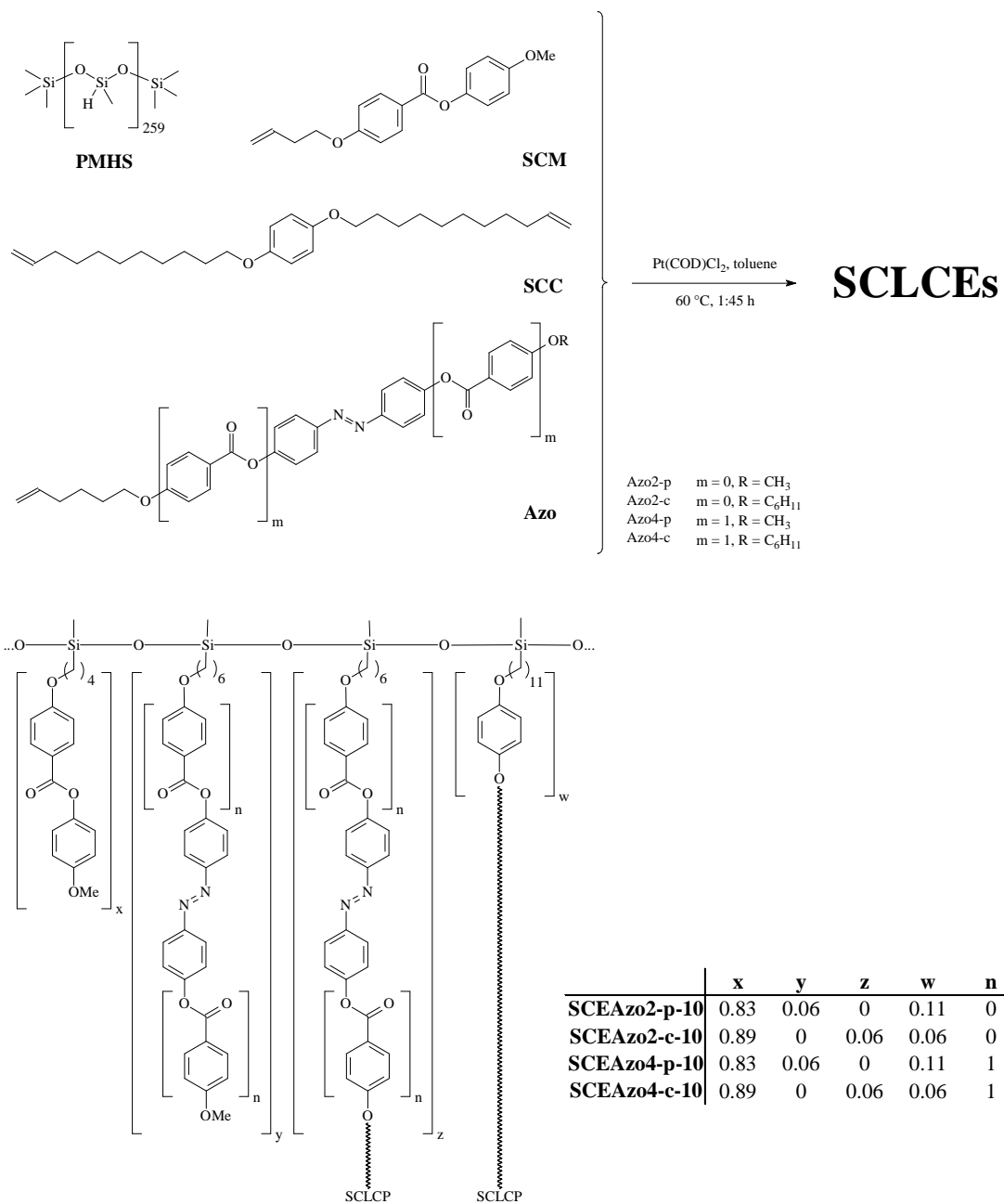### Synthesis of (E)-4,4'-bis[4-(hex-5-en-1-yloxy)benzoyloxy]azobenzene (Azo4-c)

In a 100 mL round-bottomed flask 1.00 g (4.54 mmol) of 4-(hex-5-en-1-yloxy)benzoic acid (HOBA), 1.03 g (4.99 mmol) of N,N'-dicyclohexylcarbodiimide (DCC) and 55 mg (0.45 mmol) of 4-dimethylaminopyridine (DMAP) were placed. After 30 min of stirring and purging with nitrogen, 10 mL of anhydrous CH_2Cl_2 were added. In another 25 mL flask 0.486 g (2.27 mmol) of (E)-4,4'-dihydroxy-azobenzene (DHAB) were weighted and dissolved in 10 mL of anhydrous THF under nitrogen atmosphere, and then the solution was transferred by canula to the first flask. The reaction was stirred at room temperature for 5 h until TLC (SiO$_2$, CH_2Cl_2) showed that reaction was complete. The urea derivative was filtered off, and the reaction mixture was diluted with 2 M NaOH, and extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous sodium sulphate, filtered and evaporated. The residue was chromatographed on a silica gel column with CH_2Cl_2 as eluting solvent. Yield: 1.34 g (96%).

^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.16 (4H, d, o-Ar, J=9.1 Hz), 8.00 (4H, d, o-Ar', J=8.4 Hz), 7.20 (4H, d, m-Ar, J=9.1 Hz), 6.99 (4H, d, m-Ar', J=8.4 Hz), 5.85 (2H, ddt, C$\underline{H}$=CH$_2$, J=16.9 Hz, J=10.4 Hz, J=6.7 Hz), 5.06 (2H, ddt, cis-CH=C$\underline{H}_2$, J=17.3 Hz, J=2.0 Hz, J=1.6 Hz), 5.00 (2H, ddt, $trans$-CH=C$\underline{H}_2$, J=10.2 Hz, J=2.0 Hz, J=1.0 Hz), 4.07 (4H, t, CH$_2$O, J=6.3 Hz), 2.13 (4H, tdt, CH$_2$, J=7.3 Hz, J=6.9 Hz, J=1.2 Hz), 1.85 (4H, tt, CH$_2$, J=6.9 Hz, J=6.5 Hz), 1.55 (4H, tt, CH$_2$, J=7.1 Hz, J=6.7 Hz) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 164.8 (2C, COO), 163.9 (2C, ArOCH$_2$), 153.4 (2C, Ar'OCH$_2$), 150.4 (2C, ArN=N), 138.6 (2C, $\underline{C}$H=CH$_2$), 132.6 (4C, o-Ar'H), 124.3 (4C, o-ArH), 122.7 (4C, m-Ar'H), 121.9 (2C, ArCOO), 115.4 (2C, CH=$\underline{C}$H$_2$), 114.6 (4C, m-ArH), 69.6 (2C, CH$_2$O), 33.0 (2C, CH$_2$), 28.7 (2C, CH$_2$), 25.5 (2C, CH$_2$) ppm. FTIR (NaCl): 1732 (st, C=O), 1606 (st, C=CH$_2$), 1508 (st, N=N), 1259 (st, C-O), 1174 (st, C-O), 916 (δ oop, CH=CH$_2$) cm^{-1}. UV (EtOH, 25 °C): λ_{max} = 327, 437 nm (ε =

23000, 1000 L·mol^{-1}·cm^{-1}). m.p.: C 123 SmC 157 I °C. $C_{38}H_{38}N_2O_6$ – 618,72: Calcd. C 73.77, H 6.19, N 4.53, O 15.52; Found C 73.81, H 6.19, N 4.50.

PMHS   SCM

SCC

$\xrightarrow[\text{60 °C, 1:45 h}]{\text{Pt(COD)Cl}_2\text{, toluene}}$ **SCLCEs**

Azo

Azo2-p	m = 0, R = CH₃
Azo2-c	m = 0, R = C₆H₁₁
Azo4-p	m = 1, R = CH₃
Azo4-c	m = 1, R = C₆H₁₁

	x	y	z	w	n
SCEAzo2-p-10	0.83	0.06	0	0.11	0
SCEAzo2-c-10	0.89	0	0.06	0.06	0
SCEAzo4-p-10	0.83	0.06	0	0.11	1
SCEAzo4-c-10	0.89	0	0.06	0.06	1

Scheme SI-2. Synthetic route for the four side-chain liquid-crystalline elastomers: SCEAzo2-p-10, SCEAzo2-c-10, SCEAzo4-p-10, and SCEAzo4-c-10.

Synthesis of side-chain liquid-crystalline elastomers (SCLCEs)

In a 5 mL flask, the side-chain mesogen (SCM) 4-methoxyphenyl 4-(but-3-en-1-yloxy)benzoate, the azobenzene derivative (Azo2-p, Azo2-c, Azo4-p or Azo4-c), the isotropic side-chain crosslinker (SCC) 1,4-bis(undec-10-en-1-yloxy)benzene, and poly(methylhydrosiloxane) (PMHS, DP = 259) were placed. To this mixture, 1 mL of tiophene-free toluene and 20 µL of 1 %-Pt cyclooctadieneplatinum(II) chloride, Pt(COD)Cl$_2$, in dichloromethane were added. The mixture was placed in the spinning Teflon cell form which was heated at 60 °C for 1 h 45 min at 5000 rpm.

Afterward, the reactor was cooled and the elastomer was removed from the wall. Some loads were applied in order to align the sample during the deswelling process. In this first step the elastomer is not totally crosslinked. In order to fix this orientation, the crosslinking reaction was completed by leaving the elastomer in the oven under vacuum at 60 °C for 2 days.

SCEAzo2-p-10
DSC (10 K·min^{-1}, N$_2$): T_g -4 (0.3) N 70 (1.8) I; X-ray: S = 0.74, d_m = 4.4 Å; Swelling: q = 3.5; λ_{max} = 381 nm

SCEAzo2-c-10
DSC (10 K·min^{-1}, N$_2$): T_g -2 (0.3) N 82 (2.5) I; X-ray: S = 0.76, d_m = 4.4 Å; Swelling: q = 3.1; λ_{max} = 382 nm

SCEAzo4-p-10
DSC (10 K·min^{-1}, N$_2$): T_g -2 (0.3) N 82 (1.2) I; X-ray: S = 0.76, d_m = 4.4 Å; Swelling: q = 3.3; λ_{max} = 358 nm

SCEAzo4-c-10
DSC (10 K·min^{-1}, N$_2$): T_g 8 (0.3) N 107 (0.7) I; X-ray: S = 0.77, d_m = 4.5 Å; Swelling: q = 3.1; λ_{max} = 357 nm

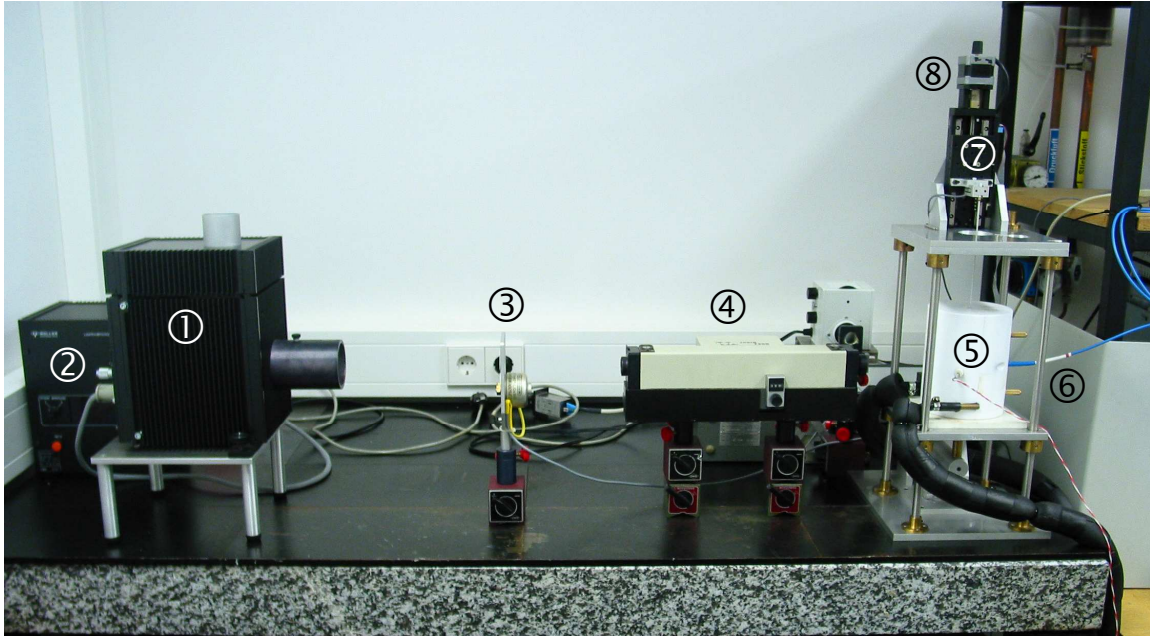*Figure SI-1*. Opto-mechanical set-up: 1) housing lamp, 2) light source, 3) chopper, 4) monochromator, 5) thermostated cell (sample), 6) spectrophotometer, 7) load cell, and 8) step motor
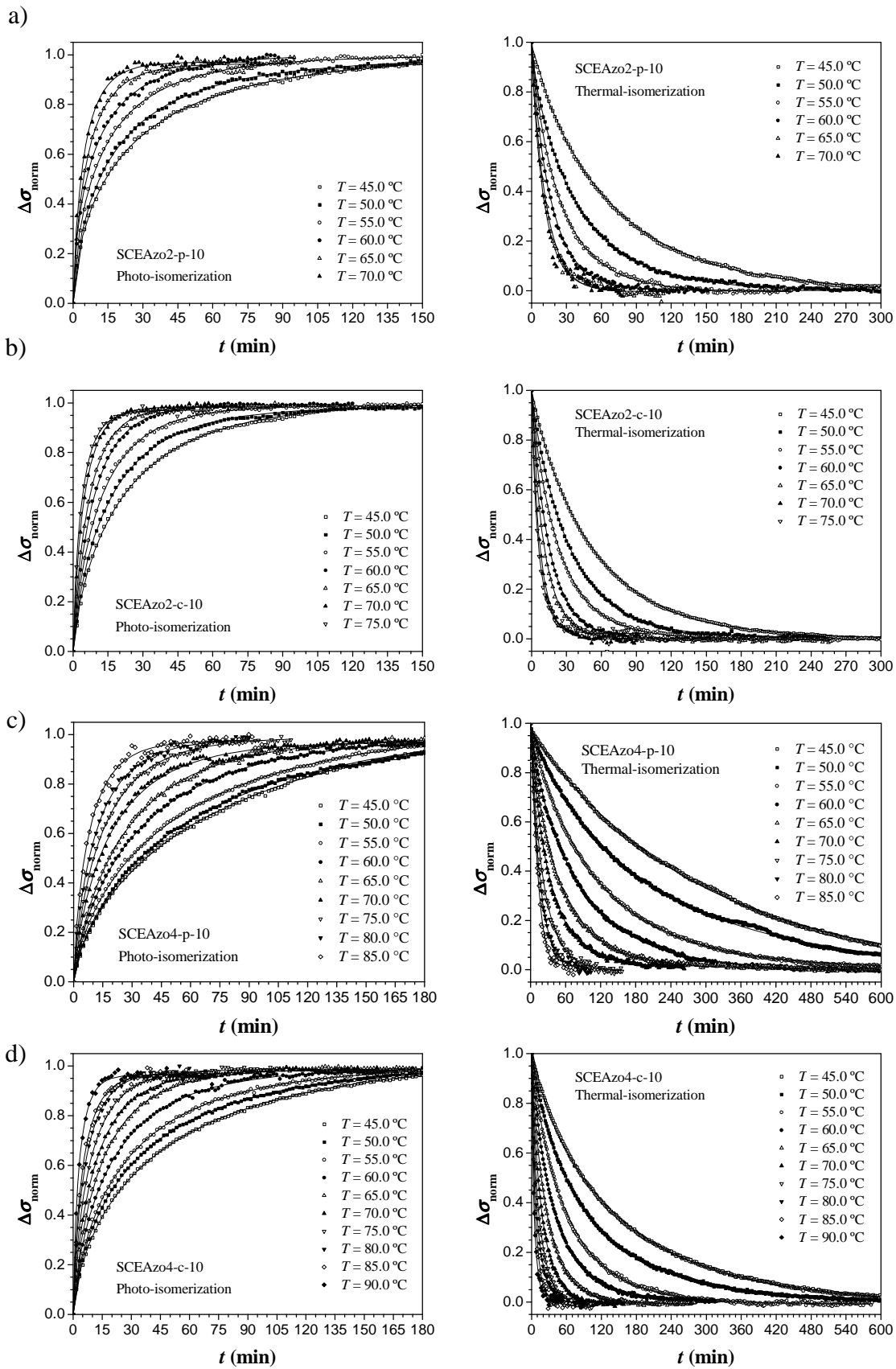
Figure SI-2. Normalized opto-mechanical curves during the photo-isomerization (left) and the thermal-isomerization (right) processes of all four elastomeric samples: a) SCEAzo2-p-10, b) SCEAzo2-c-10, c) SCEAzo4-p-10, and d) SCEAzo4-c-10.

Table SI-1a. Maximum response ($\Delta\sigma_{max}$), pre-load ($\Delta\sigma_0$), lifetime (τ_{photo}), kinetic constant (k_{photo}), exponential factor (β_{photo}) and correlation factor (R) during the photo-isomerization process for the sample SCEAzo2-p-10 at different temperatures.

T	$\Delta\sigma_{max}$	$\Delta\sigma_0$	τ_{photo}	k_{photo}	β_{photo}	R
°C	Pa	Pa	s	s^{-1}		
45.0	11432 ± 4	11470	1528 ± 2	$6.54\times10^{-4} \pm 1\times10^{-6}$	0.643 ± 0.001	0.9997
50.0	11994 ± 6	11547	1149 ± 3	$8.71\times10^{-4} \pm 2\times10^{-6}$	0.672 ± 0.002	0.998
55.0	12391 ± 5	11155	842 ± 2	$1.19\times10^{-3} \pm 3\times10^{-6}$	0.686 ± 0.002	0.9993
60.0	12690 ± 13	11146	616 ± 3	$1.62\times10^{-3} \pm 1\times10^{-5}$	0.670 ± 0.003	0.999
65.0	11812 ± 11	10529	413 ± 3	$2.42\times10^{-3} \pm 1\times10^{-5}$	0.78 ± 0.01	0.996
70.0	9165 ± 9	10176	307 ± 2	$3.26\times10^{-3} \pm 2\times10^{-5}$	0.79 ± 0.01	0.995
75.0	6573 ± 10	10091	190 ± 4	$5.30\times10^{-3} \pm 1\times10^{-4}$	0.55 ± 0.01	0.97

Table SI-1b. Maximum response ($\Delta\sigma_{max}$), pre-load ($\Delta\sigma_0$), lifetime (τ_{photo}), kinetic constant (k_{photo}), exponential factor (β_{photo}) and correlation factor (R) during the photo-isomerization process for the sample SCEAzo2-c-10 at different temperatures.

T	$\Delta\sigma_{max}$	$\Delta\sigma_0$	τ_{photo}	k_{photo}	β_{photo}	R
°C	Pa	Pa	s	s^{-1}		
45.0	38152 ± 16	13747	1340 ± 2	$7.46\times10^{-4} \pm 1\times10^{-6}$	0.754 ± 0.001	0.9996
50.0	34167 ± 12	14538	997 ± 2	$1.00\times10^{-3} \pm 2\times10^{-6}$	0.790 ± 0.002	0.9993
55.0	30807 ± 10	13860	748 ± 1	$1.34\times10^{-3} \pm 3\times10^{-6}$	0.811 ± 0.002	0.9994
60.0	27477 ± 7	13895	556 ± 1	$1.80\times10^{-3} \pm 3\times10^{-6}$	0.865 ± 0.002	0.9996
65.0	24608 ± 9	12971	433 ± 1	$2.31\times10^{-3} \pm 1\times10^{-5}$	0.877 ± 0.003	0.9994
70.0	20462 ± 10	13769	305 ± 1	$3.28\times10^{-3} \pm 1\times10^{-5}$	0.883 ± 0.004	0.998
75.0	16691 ± 12	13510	243 ± 1	$4.11\times10^{-3} \pm 2\times10^{-5}$	0.85 ± 0.01	0.998
80.0	12379 ± 35	11231	177 ± 3	$5.70\times10^{-3} \pm 1\times10^{-4}$	0.81 ± 0.01	0.994

Table SI-1c. Maximum response ($\Delta\sigma_{max}$), pre-load ($\Delta\sigma_0$), lifetime (τ_{photo}), kinetic constant (k_{photo}), exponential factor (β_{photo}) and correlation factor (R) during the photo-isomerization process for the sample SCEAzo4-p-10 at different temperatures.

T	$\Delta\sigma_{max}$	$\Delta\sigma_0$	τ_{photo}	k_{photo}	β_{photo}	R
°C	Pa	Pa	s	s^{-1}		
45.0	9353 ± 14	8895	4881 ± 21	2.05×10^{-4} ± 1×10^{-6}	0.693 ± 0.001	0.9997
50.0	9480 ± 14	8991	3826 ± 16	2.61×10^{-4} ± 1×10^{-6}	0.721 ± 0.002	0.9995
55.0	9898 ± 7	8909	3231 ± 7	3.10×10^{-4} ± 1×10^{-6}	0.717 ± 0.001	0.9998
60.0	9706 ± 4	8494	2128 ± 3	4.70×10^{-4} ± 1×10^{-6}	0.761 ± 0.001	0.9997
65.0	9504 ± 3	8530	1680 ± 2	5.95×10^{-4} ± 1×10^{-6}	0.815 ± 0.001	0.9995
70.0	8727 ± 5	8123	1208 ± 4	8.28×10^{-4} ± 3×10^{-6}	0.798 ± 0.003	0.998
75.0	8094 ± 7	7786	956 ± 3	1.05×10^{-3} ± 3×10^{-6}	0.816 ± 0.003	0.9991
80.0	6861 ± 8	7547	742 ± 3	1.35×10^{-3} ± 1×10^{-5}	0.808 ± 0.004	0.9990
85.0	5553 ± 6	7042	513 ± 3	1.95×10^{-3} ± 1×10^{-5}	0.81 ± 0.01	0.996

Table SI-1d. Maximum response ($\Delta\sigma_{max}$), pre-load ($\Delta\sigma_0$), lifetime (τ_{photo}), kinetic constant (k_{photo}), exponential factor (β_{photo}) and correlation factor (R) during the photo-isomerization process for the sample SCEAzo4-c-10 at different temperatures.

T	$\Delta\sigma_{max}$	$\Delta\sigma_0$	τ_{photo}	k_{photo}	β_{photo}	R
°C	Pa	Pa	s	s^{-1}		
45.0	29559 ± 14	10776	2759 ± 4	3.62×10^{-4} ± 1×10^{-6}	0.676 ± 0.001	0.9999
50.0	31341 ± 12	11987	2118 ± 3	4.72×10^{-4} ± 1×10^{-6}	0.697 ± 0.001	0.9998
55.0	29252 ± 9	12653	1741 ± 2	5.74×10^{-4} ± 1×10^{-6}	0.720 ± 0.001	0.9998
60.0	24482 ± 6	12107	1261 ± 2	7.93×10^{-4} ± 1×10^{-6}	0.755 ± 0.001	0.9995
65.0	21317 ± 5	11825	956 ± 1	1.05×10^{-3} ± 1×10^{-6}	0.779 ± 0.001	0.9998
70.0	18217 ± 6	11915	733 ± 1	1.37×10^{-3} ± 1×10^{-6}	0.803 ± 0.002	0.9993
75.0	15929 ± 7	12341	553 ± 1	1.81×10^{-3} ± 1×10^{-5}	0.792 ± 0.003	0.9992
80.0	13774 ± 13	11820	409 ± 2	2.44×10^{-3} ± 1×10^{-5}	0.81 ± 0.01	0.998
85.0	11920 ± 12	11822	334 ± 2	2.99×10^{-3} ± 1×10^{-5}	0.81 ± 0.01	0.997
90.0	9994 ± 7	10719	207 ± 1	4.84×10^{-3} ± 1×10^{-5}	0.83 ± 0.01	0.996
95.0	8446 ± 17	12378	160 ± 2	6.20×10^{-3} ± 1×10^{-4}	0.77 ± 0.01	0.991

Table SI-2a. Maximum response ($\Delta\sigma_{\mathrm{max}}$), pre-load ($\Delta\sigma_0$), lifetime ($\tau_{\mathrm{thermal}}$), kinetic constant ($k_{\mathrm{thermal}}$), exponential factor ($\beta_{\mathrm{thermal}}$) and correlation factor (R) during the thermal-isomerization process for the sample SCEAzo2-p-10 at different temperatures.

T	$\Delta\sigma_{\mathrm{max}}$	$\Delta\sigma_0$	τ_{thermal}	k_{thermal}	β_{thermal}	R
°C	Pa	Pa	s	s^{-1}		
45.0	10617 ± 9	11724	3912 ± 5	$2.56\times10^{-4} \pm 3\times10^{-7}$	0.897 ± 0.001	0.99993
50.0	10254 ± 15	12687	2319 ± 5	$4.31\times10^{-4} \pm 1\times10^{-6}$	0.865 ± 0.002	0.9996
55.0	11391 ± 23	11815	1420 ± 4	$7.04\times10^{-4} \pm 2\times10^{-6}$	0.837 ± 0.003	0.9995
60.0	11317 ± 29	11959	975 ± 4	$1.03\times10^{-3} \pm 4\times10^{-6}$	0.898 ± 0.004	0.9994
65.0	11203 ± 70	11180	641 ± 6	$1.56\times10^{-3} \pm 2\times10^{-5}$	0.96 ± 0.01	0.997
70.0	8648 ± 89	10189	429 ± 9	$2.33\times10^{-3} \pm 5\times10^{-5}$	0.90 ± 0.02	0.995
75.0	5315 ± 80	7476	258 ± 13	$3.90\times10^{-3} \pm 2\times10^{-4}$	0.79 ± 0.01	0.94

Table SI-2b. Maximum response ($\Delta\sigma_{\mathrm{max}}$), pre-load ($\Delta\sigma_0$), lifetime ($\tau_{\mathrm{thermal}}$), kinetic constant ($k_{\mathrm{thermal}}$), exponential factor ($\beta_{\mathrm{thermal}}$) and correlation factor (R) during the thermal-isomerization process for the sample SCEAzo2-c-10 at different temperatures.

T	$\Delta\sigma_{\mathrm{max}}$	$\Delta\sigma_0$	τ_{thermal}	k_{thermal}	β_{thermal}	R
°C	Pa	Pa	s	s^{-1}		
45.0	37449 ± 20	13643	3090 ± 2	$3.24\times10^{-4} \pm 2\times10^{-7}$	0.922 ± 0.001	0.99993
50.0	33251 ± 41	15174	1981 ± 3	$5.05\times10^{-4} \pm 8\times10^{-7}$	0.931 ± 0.002	0.9998
55.0	30720 ± 37	13870	1377 ± 2	$7.26\times10^{-4} \pm 1\times10^{-6}$	0.875 ± 0.002	0.9998
60.0	27077 ± 41	14083	902 ± 2	$1.11\times10^{-3} \pm 2\times10^{-6}$	0.914 ± 0.002	0.9998
65.0	23712 ± 68	13504	624 ± 3	$1.60\times10^{-3} \pm 1\times10^{-5}$	0.860 ± 0.004	0.9994
70.0	19602 ± 85	14188	434 ± 3	$2.30\times10^{-3} \pm 2\times10^{-5}$	0.869 ± 0.003	0.9990
75.0	16734 ± 153	13480	344 ± 5	$2.91\times10^{-3} \pm 4\times10^{-5}$	0.84 ± 0.01	0.995
80.0	11482 ± 330	11349	239 ± 8	$4.20\times10^{-3} \pm 1\times10^{-4}$	0.92 ± 0.05	0.993

Table SI-2c. Maximum response ($\Delta\sigma_{max}$), pre-load ($\Delta\sigma_0$), lifetime ($\tau_{thermal}$), kinetic constant ($k_{thermal}$), exponential factor ($\beta_{thermal}$) and correlation factor (R) during the thermal-isomerization process for the sample SCEAzo4-p-10 at different temperatures.

T	$\Delta\sigma_{max}$	$\Delta\sigma_0$	$\tau_{thermal}$	$k_{thermal}$	$\beta_{thermal}$	R
°C	Pa	Pa	s	s^{-1}		
45.0	7830 ± 6	8940	17351 ± 13	$5.80\times10^{-5} \pm 1\times10^{-7}$	0.984 ± 0.001	0.9997
50.0	8690 ± 8	8997	11789 ± 11	$8.50\times10^{-5} \pm 1\times10^{-7}$	0.847 ± 0.001	0.9997
55.0	8772 ± 6	9280	6822 ± 5	$1.47\times10^{-4} \pm 1\times10^{-7}$	0.892 ± 0.001	0.9998
60.0	9173 ± 9	8703	4777 ± 6	$2.09\times10^{-4} \pm 3\times10^{-7}$	0.847 ± 0.001	0.9997
65.0	9371 ± 12	8763	2789 ± 6	$3.59\times10^{-4} \pm 1\times10^{-6}$	0.818 ± 0.002	0.9995
70.0	8910 ± 21	7991	1881 ± 6	$5.32\times10^{-4} \pm 2\times10^{-6}$	0.849 ± 0.003	0.9993
75.0	8073 ± 30	7816	1291 ± 6	$7.75\times10^{-4} \pm 4\times10^{-6}$	0.89 ± 0.01	0.9990
80.0	6706 ± 30	7606	963 ± 6	$1.04\times10^{-3} \pm 1\times10^{-5}$	0.97 ± 0.01	0.9990
85.0	4807 ± 32	7358	813 ± 6	$1.23\times10^{-3} \pm 1\times10^{-5}$	1.25 ± 0.02	0.997

Table SI-2d. Maximum response ($\Delta\sigma_{max}$), pre-load ($\Delta\sigma_0$), lifetime ($\tau_{thermal}$), kinetic constant ($k_{thermal}$), exponential factor ($\beta_{thermal}$) and correlation factor (R) during the thermal-isomerization process for the sample SCEAzo4-c-10 at different temperatures.

T	$\Delta\sigma_{max}$	$\Delta\sigma_0$	$\tau_{thermal}$	$k_{thermal}$	$\beta_{thermal}$	R
°C	Pa	Pa	s	s^{-1}		
45.0	35571 ± 24	3709	8277 ± 7	$1.21\times10^{-4} \pm 1\times10^{-7}$	0.817 ± 0.001	0.9999
50.0	33477 ± 23	9703	5492 ± 5	$1.82\times10^{-4} \pm 2\times10^{-7}$	0.800 ± 0.001	0.9998
55.0	29020 ± 29	12653	3471 ± 5	$2.88\times10^{-4} \pm 4\times10^{-7}$	0.853 ± 0.001	0.9997
60.0	25662 ± 27	10760	2313 ± 3	$4.32\times10^{-4} \pm 1\times10^{-6}$	0.853 ± 0.001	0.9998
65.0	22207 ± 27	10628	1535 ± 3	$6.52\times10^{-4} \pm 1\times10^{-6}$	0.856 ± 0.002	0.9998
70.0	18804 ± 40	11352	1054 ± 3	$9.49\times10^{-4} \pm 3\times10^{-6}$	0.853 ± 0.003	0.9996
75.0	16585 ± 52	11879	720 ± 3	$1.39\times10^{-3} \pm 1\times10^{-5}$	0.791 ± 0.004	0.9995
80.0	14274 ± 63	11418	524 ± 4	$1.91\times10^{-3} \pm 1\times10^{-5}$	0.78 ± 0.01	0.9990
85.0	12401 ± 125	11488	405 ± 6	$2.47\times10^{-3} \pm 4\times10^{-5}$	0.80 ± 0.01	0.996
90.0	10249 ± 95	10435	234 ± 4	$4.30\times10^{-3} \pm 1\times10^{-4}$	0.82 ± 0.01	0.997
95.0	10359 ± 107	9054	182 ± 9	$5.50\times10^{-3} \pm 3\times10^{-4}$	0.79 ± 0.01	0.997

Table SI-3a. Lifetimes (τ_{photo} and τ_{thermal}), kinetic constants (k_1 and k_2), half lifetimes ($t_{1/2,\text{photo}}$ and $t_{1/2,\text{thermal}}$) and *cis*-isomer population (ϕ_{cis}) for the sample SCEAzo2-p-10 at different inverse temperatures.

$\dfrac{1/T}{\mathbf{K^{-1}}}$	$\dfrac{\tau_{\text{photo}}}{\mathbf{s}}$	$\dfrac{\tau_{\text{thermal}}}{\mathbf{s}}$	$\dfrac{k_1}{\mathbf{s^{-1}}}$	$\dfrac{k_2}{\mathbf{s^{-1}}}$	$\dfrac{t_{1/2,\text{photo}}}{\mathbf{min}}$	$\dfrac{t_{1/2,\text{thermal}}}{\mathbf{min}}$	ϕ_{cis}
0.00314	1528	3912	0.00040	0.00026	17.7	45.2	0.61
0.00310	1149	2319	0.00044	0.00043	13.3	26.8	0.50
0.00305	842	1420	0.00048	0.00070	9.7	16.4	0.41
0.00301	616	975	0.00060	0.00103	7.1	11.3	0.37
0.00297	413	641	0.00086	0.00156	4.8	7.4	0.36
0.00292	307	429	0.00093	0.00233	3.5	5.0	0.28
0.00288	190	258	0.00140	0.00388	2.2	3.0	0.26

Table SI-3b. Lifetimes (τ_{photo} and τ_{thermal}), kinetic constants (k_1 and k_2), half lifetimes ($t_{1/2,\text{photo}}$ and $t_{1/2,\text{thermal}}$) and *cis*-isomer population (ϕ_{cis}) for the sample SCEAzo2-c-10 at different inverse temperatures.

$\dfrac{1/T}{\mathbf{K^{-1}}}$	$\dfrac{\tau_{\text{photo}}}{\mathbf{s}}$	$\dfrac{\tau_{\text{thermal}}}{\mathbf{s}}$	$\dfrac{k_1}{\mathbf{s^{-1}}}$	$\dfrac{k_2}{\mathbf{s^{-1}}}$	$\dfrac{t_{1/2,\text{photo}}}{\mathbf{min}}$	$\dfrac{t_{1/2,\text{thermal}}}{\mathbf{min}}$	ϕ_{cis}
0.00314	1340	3090	0.00042	0.00032	15.5	35.7	0.57
0.00310	997	1981	0.00050	0.00050	11.5	22.9	0.50
0.00305	748	1377	0.00061	0.00073	8.6	15.9	0.46
0.00301	556	902	0.00069	0.00111	6.4	10.4	0.38
0.00297	433	624	0.00071	0.00160	5.0	7.2	0.31
0.00292	305	434	0.00097	0.00230	3.5	5.0	0.30
0.00288	243	344	0.00120	0.00291	2.8	4.0	0.29
0.00284	177	239	0.00147	0.00419	2.0	2.8	0.26

Table SI-3c. Lifetimes (τ_{photo} and $\tau_{thermal}$), kinetic constants (k_1 and k_2), half lifetimes ($t_{1/2,photo}$ and $t_{1/2,thermal}$) and *cis*-isomer population (ϕ_{cis}) for the sample SCEAzo4-p-10 at different inverse temperatures.

$1/T$	τ_{photo}	$\tau_{thermal}$	k_1	k_2	$t_{1/2,photo}$	$t_{1/2,thermal}$	ϕ_{cis}
K^{-1}	s	s	s^{-1}	s^{-1}	min	min	
0.00314	4881	17351	0.00015	0.00006	56.4	200.5	0.72
0.00310	3826	11789	0.00018	0.00008	44.2	136.2	0.68
0.00305	3231	6822	0.00016	0.00015	37.3	78.8	0.55
0.00301	2128	4777	0.00026	0.00021	24.6	55.2	0.53
0.00297	1680	2789	0.00024	0.00036	19.4	32.2	0.40
0.00292	1208	1881	0.00030	0.00053	14.0	21.7	0.36
0.00288	956	1291	0.00027	0.00077	11.0	14.9	0.26
0.00284	742	963	0.00031	0.00104	8.6	11.1	0.23
0.00281	513	813	0.00072	0.00123	5.9	9.4	0.20

Table SI-3d. Lifetimes (τ_{photo} and $\tau_{thermal}$), kinetic constants (k_1 and k_2), half lifetimes ($t_{1/2,photo}$ and $t_{1/2,thermal}$) and *cis*-isomer population (ϕ_{cis}) for the sample SCEAzo4-c-10 at different inverse temperatures.

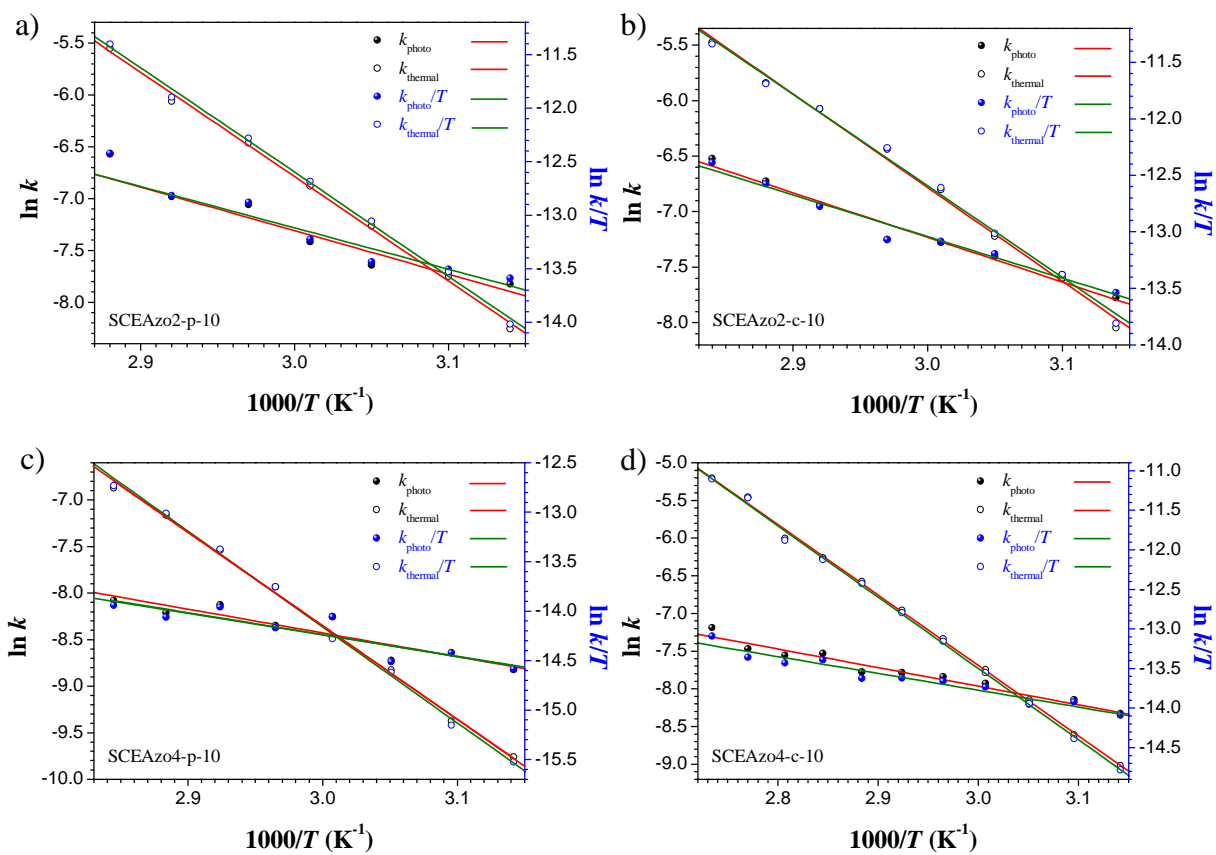| $1/T$	τ_{photo}	$\tau_{thermal}$	k_1	k_2	$t_{1/2,photo}$	$t_{1/2,thermal}$	ϕ_{cis}
K^{-1}	s	s	s^{-1}	s^{-1}	*min*	*min*	
0.00314	2759	8277	0.00024	0.00012	31.9	95.6	0.67
0.00310	2118	5492	0.00029	0.00018	24.5	63.5	0.61
0.00305	1741	3471	0.00029	0.00029	20.1	40.1	0.50
0.00301	1261	2313	0.00036	0.00043	14.6	26.7	0.45
0.00297	956	1535	0.00039	0.00065	11.0	17.7	0.38
0.00292	733	1054	0.00042	0.00095	8.5	12.2	0.30
0.00288	553	720	0.00042	0.00139	6.4	8.3	0.23
0.00284	409	524	0.00054	0.00191	4.7	6.1	0.22
0.00281	334	405	0.00052	0.00247	3.9	4.7	0.18
0.00277	207	234	0.00057	0.00427	2.4	2.7	0.12
0.00273	160	182	0.00075	0.00549	1.8	2.1	0.09

Figure SI-3. Arrhenius (black symbols and red fitting curves) and Eyring (blue symbols and green fitting curves) plots for the photo- (k_{photo}) and thermal-isomerization ($k_{thermal}$) processes of all four elastomeric samples: a) SCEAzo2-p-10, b) SCEAzo2-c-10, c) SCEAzo4-p-10, and d) SCEAzo4-c-10.

Table SI-4a. Activation energy (E_a), pre-exponential factor (A), activation enthalpy ($\Delta H^\ddagger$), activation entropy ($\Delta S^\ddagger$), and free activation enthalpy ($\Delta G^\ddagger$) of the photo-isomerization process for the sample SCEAzo2-p-10 from the Arrhenius and Eyring plots.

Sample	E_a kJ·mol^{-1}	A s^{-1}	$\Delta H^\ddagger$ kJ·mol^{-1}	$\Delta S^\ddagger$ J·mol^{-1}·K^{-1}	$\Delta G^\ddagger$ kJ·mol^{-1}
SCEAzo2-p-10	35 ± 2	$1.94\times10^2 \pm 5\times10^0$	32 ± 4	-210 ± 5	95 ± 4
SCEAzo2-c-10	33 ± 2	$1.23\times10^2 \pm 2\times10^0$	31 ± 2	-214 ± 6	95 ± 2
SCEAzo4-p-10	21 ± 4	$4.65\times10^1 \pm 5\times10^{-1}$	18 ± 4	-261 ± 5	96 ± 4
SCEAzo4-c-10	21 ± 2	$5.69\times10^1 \pm 5\times10^{-1}$	18 + 2	-259 ± 4	95 ± 2

Table SI-4b. Activation energy (E_a), pre-exponential factor (A), activation enthalpy ($\Delta H^\ddagger$), activation entropy ($\Delta S^\ddagger$), and free activation enthalpy ($\Delta G^\ddagger$) of the thermal-isomerization process for the sample SCEAzo2-p-10 from the Arrhenius and Eyring plots.

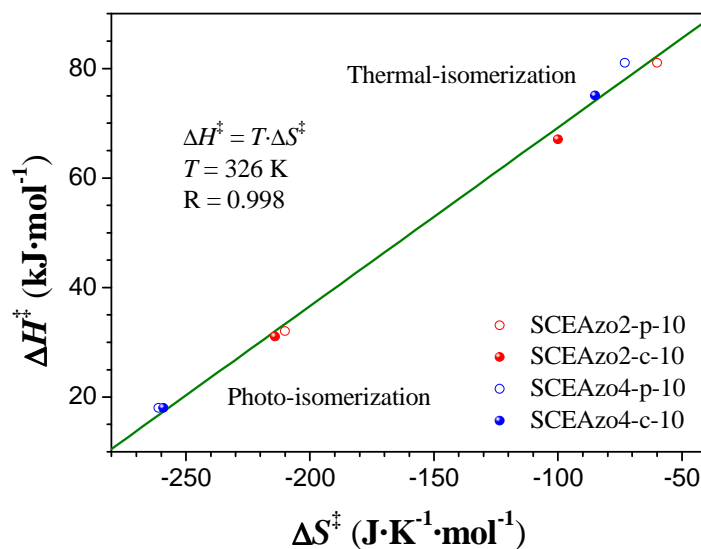| Sample	E_a kJ·mol^{-1}	A s^{-1}	$\Delta H^\ddagger$ kJ·mol^{-1}	$\Delta S^\ddagger$ J·mol^{-1}·K^{-1}	$\Delta G^\ddagger$ kJ·mol^{-1}
SCEAzo2-p-10	84 ± 2	$1.47\times10^{10} \pm 2\times10^8$	81 ± 2	-60 ± 5	99 ± 2
SCEAzo2-c-10	70 ± 2	$1.10\times10^8 \pm 4\times10^6$	67 ± 2	-100 ± 6	97 ± 2
SCEAzo4-p-10	83 ± 2	$2.78\times10^9 \pm 4\times10^7$	81 ± 2	-73 ± 5	103 ± 2
SCEAzo4-c-10	78 ± 1	$6.97\times10^8 \pm 3\times10^6$	75 ± 1	-85 ± 3	100 ± 1

Figure SI-4. Activation enthalpy ($\Delta H^{\ddagger}$) versus activation entropy ($\Delta S^{\ddagger}$) of the *trans*-to-*cis* photo-isomerization and *cis*-to-*trans* thermal-isomerization processes for all four photoactive SCLCEs.
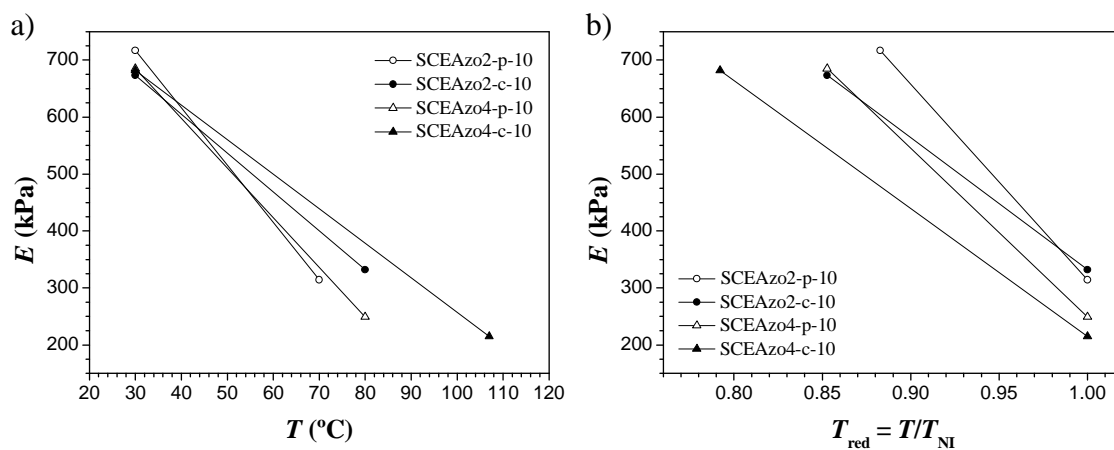

Figure SI-5. Young's moduli for the four samples in the nematic phase ($T = 30$ °C), and in the clearing temperature ($T = T_{NI}$) as function of a) the temperature, and b) of the reduced temperature.