Photoactive selectively deuterated reactive mesogens targeted for light-controlled opto-mechanical applications

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SUPPLEMENTARY INFORMATION

Synthetic experimental

All starting materials and reagents were purchased from Sigma-Aldrich, Acros Organics or Lach:Ner. All solvents used for the synthesis were "p.a." grade. Column chromatography was carried out using Merck Kieselgel 60 (60-100 μm). ^{1}H NMR spectra were recorded on Varian VNMRS 300 instrument; deuteriochloroform ($CDCl_3$) and hexadeuteriodimethyl sulfoxide (DMSO-d_6) were used as solvents and signals of the solvent served as internal standard. Chemical shifts (δ) are given in ppm and *J* values are given in Hz. Signals were identified by APT, gCOSY and gHMBCAD experiments. Elemental analyses were carried out on Elementar vario EL III instrument. The purity of all final compounds was checked by HPLC analysis (high-pressure pump ECOM Alpha; column WATREX Biospher Si 100, 250 × 4 mm, 5 μm; detector WATREX UVD 250) and were found to be >99.8 %.

N-(4-(Decyloxy)phenyl)acetamide (2).

A mixture of 4-acetamidophenol (15.0 g, 0.10 mol), 1-bromodecane (24.30 g, 0.11 mol) and potassium hydroxide (6.20 g, 0.11 mol) in 80% aqueous ethanol (400 mL) was stirred under reflux for 12 h. After cooling to room temperature, the solution was poured into water (400 mL). Precipitated *N*-(4-(decyloxy)phenyl)acetamide was filtered off, washed with water and recrystallized from ethanol. Yield 27.40 g (95 %). ^{1}H NMR ($CDCl_3$) δ: 7.35 (d, 2 H, H-2, H-6); 6.83 (d, 2 H, H-3, H-5); 3.90 (t, 2 H, CH_2O); 2.14 (s, 3 H, CH_3CO); 1.75 (2 H, q, *J* = 7.1, C**H**$_2$$CH_2O$); 1.2 - 1.5 (m, 12 H, $(CH_2)_6$), 0.88 (t, *J* = 6.7, 3 H, C**H**$_3$$CH_2$).

***4-(Decyloxy)phenylammonium-hydrogensulphate (3)*.**

N-(4-Decyloxyphenyl)acetamide (27.0 g, 0.99 mol) was suspended in sulphuric acid (250 mL, 20%) and refluxed with stirring, until the organic part was completely dissolved and clear solution formed. After cooling to room temperature, the precipitate was filtered off, washed with water and recrystallized from aqueous ethanol (70%) to yield white solid **3** (33.0 g, 98 %). ^{1}H NMR (DMSO-d_6) δ 7.43 (d, *J* = 8.5, 2 H, H-2, H-6); 7.20 (d, *J* = 8.5, 2 H, H-3, H-5); 3.96 (t, 2 H, CH_2O); 1.73 (q, *J* = 7.1, 2 H, C**H**$_2$$CH_2O$); 1.2 - 1.5 (m, 12 H, $(CH_2)_6$), 0.86 (t, *J* = 6.7, 3 H, C**H**$_3$$CH_2$).

4´-((4-(Decyloxy)phenyl)diazenyl)phenol (4a)

A solution of sodium nitrite (5.0 g, 70.0 mmol) in 10 m of water was added dropwise to a suspension of 4-(decyloxy)-phenylammonium-hydrogensulphate (17.40 g, 50.0 mmol) in glacial acetic acid (50 mL), keeping the temperature below 10 ºC. Diazotization mixture was stirred for another 30 min and then it was added portion-wise to the mixture of phenol (5.80 g, 61.62 mmol) and sodium hydroxide solution (100.0 g, 25%). The temperature of the reaction was kept below 10 °C by ice-water bath and the pH of the reaction mixture was kept in basic region by occasional addition of sodium hydroxide solution. After the last portion of diazonium salt solution, the reaction mixture was stirred for 1 h. Precipitated solid was filtered off and washed with diluted hydrochloric acid (1:5) and water. Recrystallization from ethanol yielded **4a** as orange solid (18.83 g, 95 %). M.p. 103 °C. ^{1}H NMR (DMSO-d_6) δ 10.19 (bs, 1H,-OH); 7.55 (m, 4 H, H-2, H-6, H-3´, H-5´); 7.08 (2 H, d, *J* = 8.4, H-3, H-5); 6.91 (2 H, d, *J* = 8.4, H-2´, H-6´); 4.04 (2 H, t, CH_2O); 1.73 (2 H, q, *J* = 7.1, C**H**$_2$$CH_2O$); 1.2 – 1.5 (14 H, m, $(CH_2)_7$); 0.88 (3 H, t, *J* = 6.7, C**H**$_3$$CH_2$).

4´-((4-(Decyloxy)phenyl)diazenyl)-3´,5´-dimethylphenol (4b)

Using the synthetic protocol described for **4a**: 4-(dexyloxy)-phenylammonium-hydrogensulphate (7.0 g, 20.13 mmol) in acetic acid was diazotized with sodium nitrite (1.50 g, 21.17 mmol) and then it was added portion-wise to the mixture of 3,5-dimethylphenol (2.60 g, 21.28 mmol) in sodium hydroxide (17.0 g, 0.43 mol) in water. Yield after crystallization from ethanol: 6.9 g, 85 %. M.p. 59 °C. ^{1}H NMR (DMSO-d_6) δ 9.80 (bs, 1H, -OH); 7.75 (d, 2 H, H-2, H-6); 7.07 (d, 2 H, H-3, H-5); 6.56 (s, 2 H, H-2´, H-6´); 4.04 (t, 2 H, CH_2O); 2.36 (s, 6 H, $ArCH_3$); 1.75 (2 H, quin. *J* = 7.1, C**H**$_2$$CH_2O$); 1.2 - 1.5 (m, 14 H, $(CH_2)_7$), 0.88 (t, 3 H, C**H**$_3$$CH_2$). ^{13}C NMR ($CDCl_3$) δ ppm 161.25 (C-4), 155. 11 (C-1´), 147.23 (C-1), 144.91 (C-4´), 134.24 (C-3´, C-5´), 123.99 (C-2, C-6), 115.73 (C-3, C-5), 114.81 (C-2´, C-6´), 68.34 (OCH_2), 31.56 (**C**$H_2CH_2CH_3$), 29.53 (2 × $(CH_2)_2$), 29.15 (**C**H_2CH_2O), 25.68 (**C**$H_2(CH_2)_2O$), 22.60 (**C**H_2CH_3), 19.70 (Ar(**C**$H_3)_2$), 14.05 (CH_2**C**H_3).

4-(Undec-10-enyloxy)benzoic acid (7).

A mixture of 10-undecencyl *p*-toluenesulfonate (16.0 g, 49.31 mmol), methyl 4-hydroxybenzoate (7.50 g, 49.29 mmol), anhydrous potassium carbonate (13.62 g, 98.55 mmol), and acetone (200 mL) was stirred with reflux for 8 h. The cooled mixture was poured into water (300 mL), extracted with diethylether (3 x 70 mL) and combined organic layers washed with water (2 x 30 mL). After removal of the solvent under reduced pressure, the residue was dissolved in ethanol (200 mL), heated to ca. 60 °C and solution of potassium hydroxide (6.91 g, 123.16 mmol) in ethanol (50 mL) was added with stirring. The heating was turned off and the reaction mixture was stirred for ca 1 h, while the precipitate gradually formed. Cooled mixture was poured into ice-cooled hydrochloric acid (1:2, 50 mL). The crude product was filtered off, washed with water, dried and then crystallized from ethanol to yield acid **7** (13.08 g, 91 %). M.p. 81 °C ^{1}H NMR ($CDCl_3$) δ: 8.06 (s, 2 H, H-2, H-6) 5.82 (ddt, *J*=16.95, 10.20, 6.68, 6.68 Hz, 1 H, CH=) 4.85 - 5.09 (m, 2 H, =CH_2) 4.02 (t, *J*=6.46 Hz, 2 H, CH_2O) 1.97 - 2.14 (m, 2 H, C**H**$_2$CH=) 1.72 - 1.89 (m, 2 H, C**H**$_2$$CH_2O$) 1.18 - 1.54 (m, 12 H, $(CH_2)_6$).

10HABU-D2 [4´-((4-(Decyloxy)phenyl)diazenylphenyl-4´´-(undec-10-enyl-oxy)-benzoate-3,5-d_2]

Benzoic acid **7** (2.0 g, 6.84 mmol) and phenol **4a** (2.42 g, 6.83 mmol) were dissolved in dry dichloromethane and *N,N´*-(dicyclohexyl)carbodiimide (DCC, 1.55 g, 7.36 mmol) and 4-(*N,N*-dimethylamino)pyridine (DMAP, 0.27 g, 2.19 mmol) were added. The mixture was stirred for

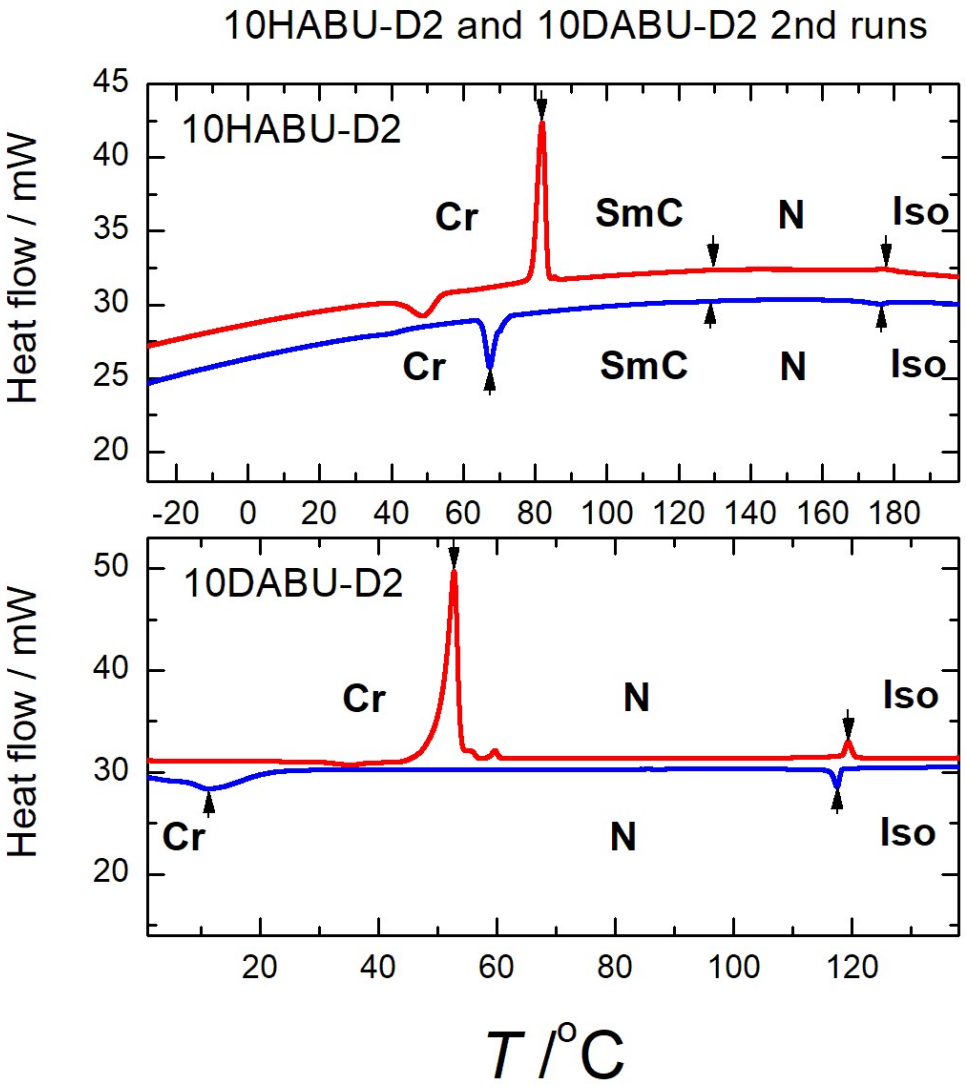
15 h under anhydrous conditions and then the precipitate was filtered off. Filtrate was evaporated and the crude product subjected to column chromatography on silica (dichloromethane). Further recrystallization from hexane yielded 3.65 g (85 %) of **10HABU-D2** as a light-orange solid. ^{1}H NMR ($CDCl_3$) δ: 8.16 (d, 2H, *J*=8.5, H-2´´, H-6´´); 7.95 (d, 2H, *J*=8.8, H-2, H-6); 7.35 (d, *J*=8.9 Hz, 2 H, H-3´, H-5´); 7.01 (d, *J*=8.9, 2 H, H-3, H-5); 5.82 (ddt, *J*=17.1, 10.3, 6.6, 6.6, 1 H, CH=); 4.89 - 5.05 (m, 2H, C**H**$_2$=CH); 4.05 (td, *J*=6.6, 2.14 Hz, 4 H, 2x CH_2O), 2.05 (q, 2H, C**H**$_2$CH=); 1.83 (quin, 4H, *J*=6.87, 2x C**H**$_2$$CH_2O$), 1.43 - 1.52 (m, 4 H, 2x C**H**$_2$$CH_2$ CH_2O), 1.21 - 1.42 (m, 22H, 11x CH_2), 0.89 (t, 3H, *J*=6.7, CH_3CH_2). ^{13}C NMR ($CDCl_3$) δ: 164.69 (s, COO), 163.58 (s, C-4´´), 161.75 (s, C-4), 152.58 (s, C-1´), 150.34 (s, C-4´), 146.77 (s, C-1), 139.19 (s, CH=), 132.23 (s, C-2´´, C-6´´), 124.75 (s, C-2, C-6), 123.69 (s, C-3´, C-5´), 122.35 (s, C-3, C-5), 121.28 (s. C-1´´), 114.71 (s, C-2´, C-6´), 114.14 (s, CH_2=), 68.38 (s, CH_2O), 68.34 (s, CH_2O), 33.79 (s, **C**H_2CH=), 31.89 (s, **C**$H_2CH_2CH_3$), 29.56 (s, CH_2), 29.55 (s, CH_2), 29.48 (s, CH_2), 29.40 (s, CH_2), 29.38 (s, CH_2), 29.33 (s, CH_2), 29.31 (s, CH_2), 29.19 (s, CH_2), 29.10 (s, CH_2), 29.08 (s, CH_2), 28.91 (s, CH_2), 26.01 (s, CH_2), 25.96 (s, CH_2), 22.67 (s, **C**H_2CH_3), 14.11 (s, CH_2**C**H_3). Anal. calcd for $C_{40}H_{52}D_2N_2O_4$: calcd C 76.39, H 8.98, N 4.45, found C 76.26, H 8.90, N 4.52 %.

10DABU-D2 (4´-((4-(Decyloxy)phenyl)diazenyl)-3´,5´-dimethylphenyl-4´´-(undec-10-enyl-oxy)-benzoate-3,5-*d*$_2$)

This compound was synthesized by the procedure reported for **10HABU-D2**. Reaction of benzoic acid **7** (2.0 g, 6.84 mmol) and phenol **4b** (2.61 g, 6.82 mmol) in dry dichloromethane in the presence of DCC (1.58 g, 7.43 mmol) and DMAP (0.27 g, 2.19 mmol), followed by the same purification procedure, gave 3.98 g (89 %) of **10DABU-D2** after the final crystallization. ^{1}H NMR ($CDCl_3$) δ: 8.14 (d, 2H, H-2´´, H-6´´); 7.88 (d, 2H, *J*=8.9, H-2, H-6); 7.01 (d, *J*=8.9, 2 H, H-3, H-5); 6.97 (s, 2 H, H-3´, H-5´); 5.82 (ddt, *J*=17.1, 10.3, 6.6, 6.6, 1 H, CH=); 4.90 - 5.04 (m, 2H, C**H**$_2$=CH); 4.05 (td, *J*=6.5, 2.3, 4 H, 2x CH_2O), 2.37 (s, 6H, 2x $ArCH_3$); 2.02 - 2.09 (m, 2 H, C**H**$_2$CH=); 1.77 - 1.88 (m, 4H, 2x C**H**$_2$$CH_2O$), 1.44 - 1.53 (m, 4 H, 2x C**H**$_2$$CH_2$ CH_2O), 1.22 - 1.43 (m, 22H, 11x CH_2), 0.89 (t, 3H, *J*=6.7, CH_3CH_2). ^{13}C NMR ($CDCl_3$) δ: 165.01 (s, COO), 163.43 (s, C-4´´), 161.74 (s, C-4), 149.87 (s, C-1´), 148.99 (s, C-1), 147.03 (s, C-4´), 139.20 (s, CH=), 132.50 (s, C-3´, C-5´), 132.15 (s, C-2´´, C-6´´), 124.31 (s, C-2, C-6), 122.00 (s, C-3, C-5), 121.56 (s. C-1´´), 114.67 (s, C-2´, C-6´), 114.14 (s, CH_2=), 68.40 (s, CH_2O), 68.31 (s, CH_2O), 33.79 (s, **C**H_2CH=), 31.89 (s, **C**$H_2CH_2CH_3$), 29.56 (s, CH_2), 29.55 (s, CH_2), 29.48 (s, CH_2), 29.40 (s, CH_2), 29.37 (s, CH_2), 29.33 (s, CH_2), 29.31 (s, CH_2), 29.17 (s, CH_2), 29.10 (s, CH_2), 29.09 (s, CH_2), 28.91 (s, CH_2),

26.00 (s, CH_2), 25.97 (s, CH_2), 22.67 (s, **C**H_2CH_3), 19.10 (s, $ArCH_3$), 14.11 (s, CH_2**C**H_3). $C_{42}H_{56}D_2N_2O_4$: calcd C 76.79, H 9.21, N 4.26, found C 76.49, H 9.29, N 4.22 %.

Figure S1. DSC curves 10HABU-D2 and 10DABU-D2 (second runs). See the main text for details.



Isomerization study

Isomerization was studied by proton NMR spectrometry in $CDCl_3$ using Varian VNMRS 300 spectrometer system. The samples of concentration 30 mmol/L were prepared in a standard NMR tube from dry oxygen-free $CDCl_3$ under argon atmosphere to prevent subsequent photolytic reaction of the solvent generating phosgene and DCl corrupting the kinetic measurements. The sample was irradiated at 25°C by UV-LED 365 nm with the intensity of 400 mW/cm^2 for one hour to assure that the photostationary state was reached. Then the sample was then transferred to the NMR spectrometer in the dark, to avoid

photoisomerization by ambient light. First photostationary state composition was determined and then the spectrometer was heated to desired temperature for the thermal Z-E isomerization measurement. An array of proton spectra in time was measured, keeping the same parameters and the kinetic data were acquired in the form of normalized integral intensities of few well-separated signals of isomers. The kinetic experiment was run to 50 °C to acquire data at reasonable amount of time and to assure the comparability of the results of both materials. See S3 for kinetic plots.

The contents of Z isomer in the photostationary state reached under the above mentioned conditions was 95 % for 10HABU-D2 and 87 % 10DABU-D2.

The first order rate constant of Z – E thermal isomerisation in $CDCl_3$ at 50 °C found for 10HABU-D2 was $1.62\pm0.16 \cdot 10^{-3}$ s^{-1} and for 10DABU-D2 was $3.26\pm0.12 \cdot 10^{-6}$ s^{-1}, see kinetic plots in Fig S3.

Figure S2. Proton NMR spectrum of 10DABU-D2 measure at 25 °C after irradiation by UV light for 15 min. It clearly shows the separation of several signals of E and Z isomers, which can be used for determination of the photostationary state composition and the evolution of the signal in time can be used to acqure kinetic data on the stability of Z isomer. Additionally, the sharp nature of the peak of (*Z*)-$ArCH_3$ gives clear evidence of the free rotation of the methylated phenyl ring.

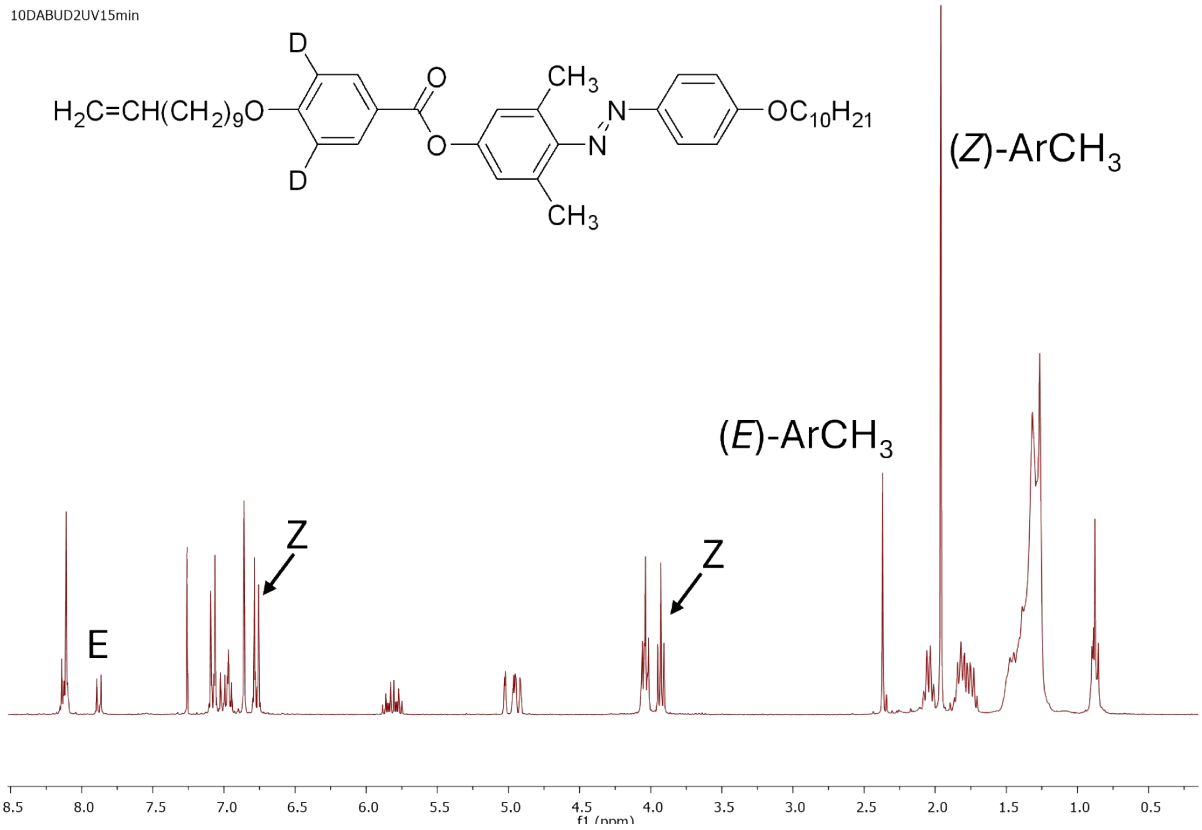
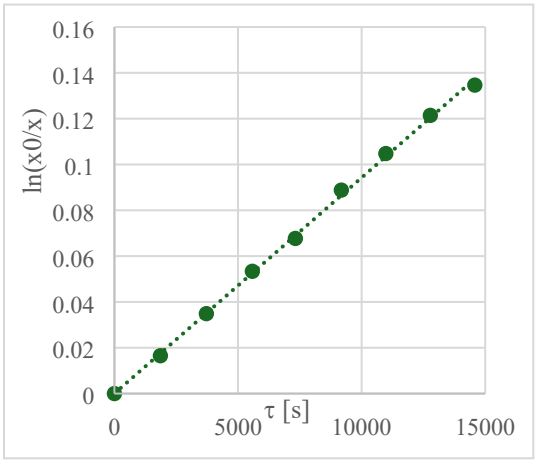
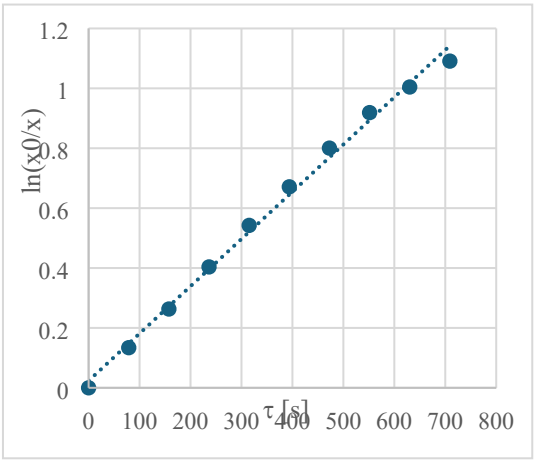


Figure S3. Kinetic plots of thermal Z-E isomerization at 50 °C in $CDCl_3$ of (a)10DABU-D2 and (b) 10HABU-D2.



(a)



(b)