Supporting information for:

Light-induced bi-directional switching of thermal conductivity in azobenzene-doped liquid crystal mesophases.

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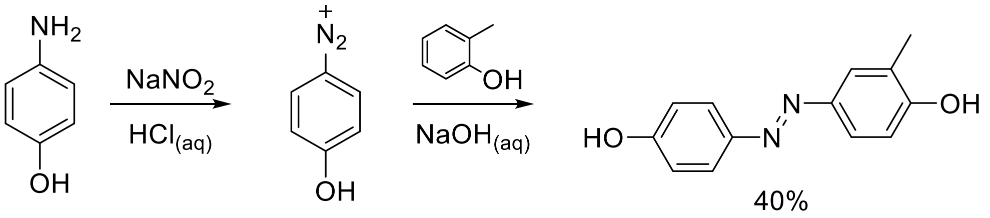
1. Experimental Procedures

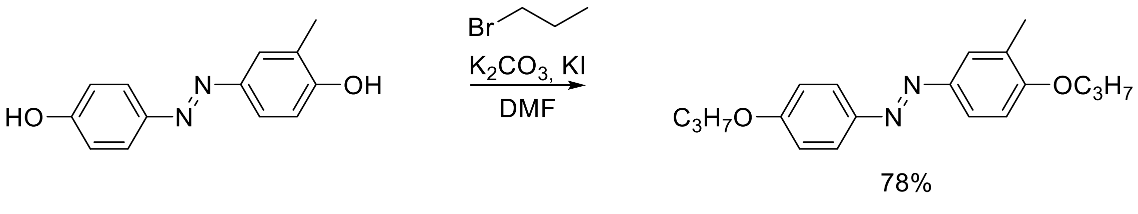
4,4'-dialkyloxy-3-methylazobenzene derivatives were synthesized following a modification of a previously described route[1].

1.1. Synthesis of 4,4'-dihydroxy-3-methylazobenzene



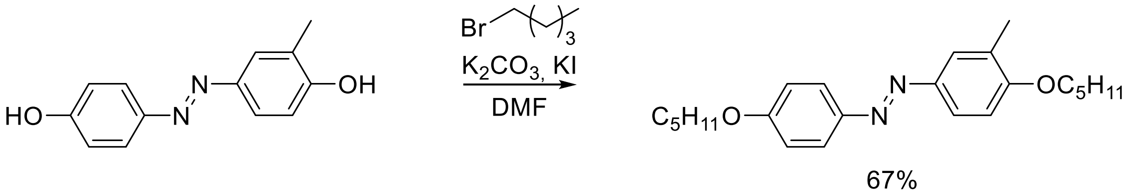
In a 100 mL round bottom flask 3.01 g of 4-aminophenol (27.49 mmol, 1.00 equiv.) were dissolved in 35.0 mL of 2.5 M $HCl_{(aq)}$, and the obtained solution was cooled in an ice bath. Over this solution, 2.27 g of $NaNO_2$ (32.99 mmol, 1.20 equiv) in 3.0 mL of deionized water were added dropwise for 5 minutes, and the mixture was stirred for 15 minutes at 0 ºC. Then, 2.97 g of *o*-cresol (27.49 mmol, 1.00 equiv.) previously dissolved in 11.0 mL of a $NaOH_{(aq)}$ solution (20%) were added slowly under stirring at 0 ºC. The mixture was allowed to reach room temperature and then stirred overnight. The reaction mixture was acidified with 1 M $HCl_{(aq)}$ and extracted with ethyl acetate (3 × 20 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and the solvent was removed under vacuum. The crude mixture was purified by flash chromatography over silica gel (1:2 ethyl acetate/hexane) to give the desired product as a brown solid (2.53 g, 40% yield). ^{1}H-RMN (300 MHz, DMSO-d_6) δ 10.08 (s, 1H), 10.04 (s, 1H), 7.70 (d, *J* = 8.23 Hz, 2H), 7.61 (s, 1H), 7.55 (d, *J* = 8.53 Hz, 1H), 6.90 (m, 3H), 2.20 (s, 3H), (**Figure S19**).

1.2. Synthesis of 4,4'-dipropyloxy-3-methylazobenzene



A mixture of 4,4'-dihydroxy-3-methylazobenzene (0.3 g, 1.31 mmol, 1.00 equiv.), 1-bromopropane (0.37 g, 3.01 mmol, 2.30 equiv.), K_2CO_3 (0.38 g, 2.75 mmol, 2.10 equiv.), and a catalytic amount of potassium iodide in 15.0 mL of N,N-dimethylformamide was heated at 70 ºC for 24 h. The reaction mixture was cooled down to room temperature and then acidified with 1 M $HCl_{(aq)}$ until precipitation of a yellow solid. The yellow solid was then isolated by filtration and washed with deionized water. The solid was dissolved in chloroform, dried over $MgSO_4$, and the solvent removed under reduced pressure. The crude material was purified by flash chromatography over silica gel (1:9 ethyl acetate/hexane) to give 4,4'-dipropyloxy-3-methylazobenzene as a yellow powder (0.32 g, 78% yield). ^{1}H-RMN (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.46 Hz, 2H), 7.74 (m, 2H), 6.99 (d, *J* = 9.27 Hz, 2H) 6.90 (d, *J* = 9.20 Hz, 1H), 4.00 (m, 4H), 2.31 (s, 3H), 1.86 (m, 4H), 1.08 (m, 6H), (**Figure S20**).

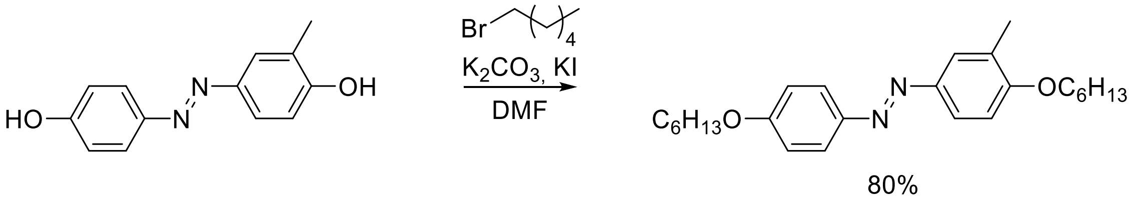
1.3. Synthesis of 4,4'-dipentyloxy-3-methylazobenzene



A mixture of 4,4'-dihydroxy-3-methylazobenzene (0.325 g, 1.42 mmol, 1.00 equiv.), 1-bromopentane (0.495 g, 3.28 mmol, 2.30 equiv.), K_2CO_3 (0.411 g, 2.98 mmol, 2.10 equiv.), and a catalytic amount of potassium iodide in 16.25 mL of N,N-dimethylformamide was heated under argon atmosphere at 95 ºC for 24 h. The reaction mixture was cooled down to room temperature and neutralized using 1 M $HCl_{(aq)}$ until an orange solid is precipitated. The orange precipitate was isolated by filtration and washed with deionized water. The solid was dissolved in dichloromethane, dried over $MgSO_4$, and the solution was concentrated under reduced pressure. The crude material was purified by gradient flash chromatography over silica gel (5:95 to 20:80 ethyl acetate/hexane) to give 4,4'-dipentyloxy-3-methylazobenzene as an orange powder (0.352 g, 67% yield). ^{1}H-RMN (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.93 Hz, 2H), 7.73 (m, 2H), 6.98 (d, *J* = 8.52 Hz, 2H), 6.90 (d, *J* = 9.26 Hz, 1H), 4.05 (m, 4H), 2.30 (s, 3H), 1.84 (m, 4H), 1.44 (m, 8H), 0.96 (m, 6H), (**Figure S21**).

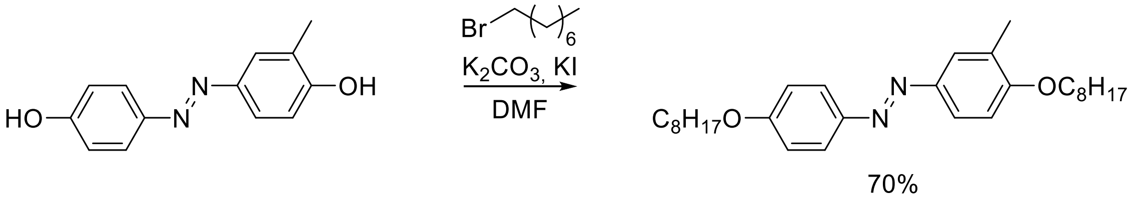
Note that when the ^{1}H-NMR spectrum is performed at room temperature, low-intensity satellite signals corresponding to the cis isomer of the azobenzene derivative appear (**Figure S22**). However, these signals completely disappear when increasing temperature due to thermal cis-trans reconversion. We have estimated the trans/cis ratio at 298 K by integrating the signals of both isomers at 4.05 and 2.30 ppm, obtaining a 10% of cis-azobenzene at room temperature.

1.4. Synthesis of 4,4'-dihexyloxy-3-methylazobenzene



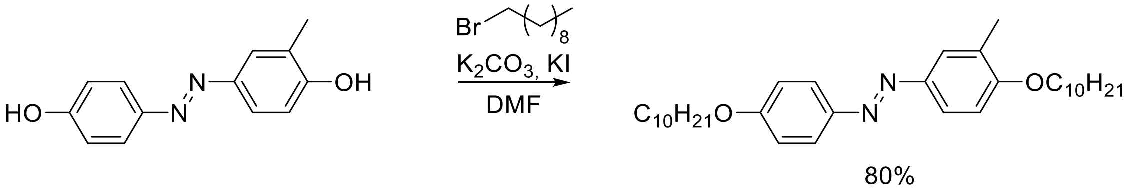
A mixture of 4,4'-dihydroxy-3-methylazobenzene (0.30 g, 1.31 mmol, 1.00 equiv.), 1-bromohexane (0.497 g, 3.01 mmol, 2.30 equiv.), K_2CO_3 (0.379 g, 2.75 mmol, 2.10 equiv.), and a catalytic amount of potassium iodide in 15 mL of N,N-dimethylformamide was heated at 120 ºC for 24 h. The reaction mixture was cooled down to room temperature and neutralized using 1 M $HCl_{(aq)}$ until an orange precipitate is obtained. The yellow precipitate was isolated by filtration and washed with deionized water. The solid was dissolved in chloroform, dried over $MgSO_4$, and the solution was concentrated under reduced pressure. The residue was recrystallized from methanol to afford 4,4'dihexyloxy-3-methylazobenzene as an orange solid (0.415 g, 80% yield). ^{1}H-RMN (300 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.86 Hz, 2H), 7.73 (m, 2H), 6.98 (d, *J* = 8.90 Hz, 2H), 6.90 (d, *J* = 9.39 Hz, 1H), 4.04 (m, 4H), 2.30 (s, 3H), 1.82 (m, 4H), 1.54 (m, 4H), 1.36 (m, 8H), 0.92 (m, 6H), (**Figure S23**).

1.5. Synthesis of 4,4'-dioctyloxy-3-methylazobenzene



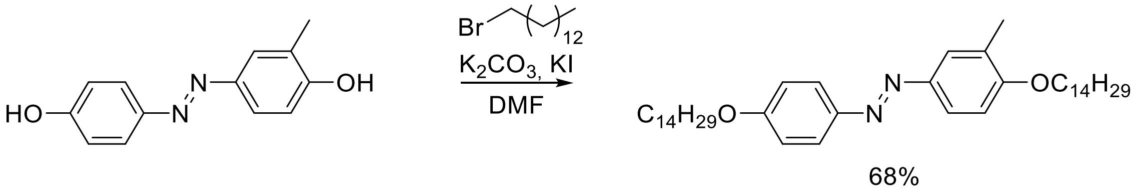
A mixture of 4,4'-dihydroxy-3-methylazobenzene (0.8 g, 3.50 mmol, 1.00 equiv.), 1-bromooctane (1.55 g, 8.05 mmol, 2.30 equiv.), K_2CO_3 (1.21 g, 8.75 mmol, 2.50 equiv.), and a catalytic amount of potassium iodide in 40 mL of N,N-dimethylformamide was heated to 100 ºC for 24 h. The reaction mixture was cooled down to room temperature, neutralized using 1 M $HCl_{(aq)}$, and the aqueous phase was extracted with diethyl ether (3 × 20 mL). The combined organic phase was washed with water (1 × 20 mL) and brine (1 × 20 mL). The organic phase was dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (1:9 diethyl ether/hexane) to give 4,4'-dioctyloxy-3-methylazobenzene as an orange solid (1.11 g, 70% yield). ^{1}H-RMN (300 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.87 Hz, 2H), 7.73 (m, 2H), 6.99 (d, *J* = 8.96 Hz, 2H), 6.90 (d, *J* = 9.40 Hz, 1H), 4.03 (m, 4H), 2.30 (s, 3H), 1.83 (m, 4H), 1.49 (m, 4H), 1.32 (m, 16H), 0.90 (m, 6H), (**Figure S24**).

1.6. Synthesis of 4,4’-didecyloxy-3-methylazobenzene



A mixture of 4,4’-dihydroxy-3-methylazobenzene (0.442 g, 1.94 mmol, 1.00 equiv.), 1-bromodecane (0.96 g, 4.36 mmol, 2.25 equiv.) and K_2CO_3 (2.15 g, 15.5 mmol, 8.00 equiv.), and a catalytic amount of potassium iodide in 24 mL of N,N-dimethylformamide was heated at 95 ºC for 24 h. The reaction mixture was cooled down to room temperature, neutralized using 1 M $HCl_{(aq)}$ and then extracted with chloroform (3 × 20 mL). The combined organic phase was washed with water (1 × 20 mL) and brine (1 × 20 mL). The organic phase was dried over $MgSO_4$ and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography over silica gel (gradient from 100% hexane to 100% ethyl acetate) to give 4,4’-didecyloxy-3-methylazobenzene as a yellow solid (0.8 g, 80% yield). ^{1}H-RMN (300 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.80 Hz, 2H), 7.73 (m, 2H), 6.98 (d, *J* = 8.95 Hz, 2H), 6.90 (d, *J* = 9.48 Hz, 1H), 4.03 (m, 4H), 2.30 (s, 3H), 1.82 (m, 4H), 1.49 (m, 4H), 1.31 (m, 24H), 0.89 (m, 6H), (**Figure S25**).

1.7. Synthesis of 4,4’-ditetradecyloxy-3-methylazobenzene



A mixture of 4,4’-dihydroxy-3-methylazobenzene (0.801 g, 3.50 mmol, 1.00 equiv.), 1-bromotetradecane (2.23 g, 8.05 mmol, 2.30 equiv.) K_2CO_3 (1.21 g, 8.75 mmol, 2.50 equiv.), and a catalytic amount of potassium iodide in 40 mL of N,N-dimethylformamide was heated at 95 ºC for 24 h. The reaction mixture was cooled to room temperature, neutralized using 1 M $HCl_{(aq)}$ and then extracted with diethyl ether (3 × 20 mL). The combined organic phase was washed with water (1 × 20 mL) and brine (1 × 20 mL). The organic phase was dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The residue was dissolved in diethyl ether/hexane (1:9) and filtrated through a short pad of silica gel to give 4,4’-ditetradecyloxy-3-methylazobenzene as an orange powder (1.48 g, 68% yield). ^{1}H-RMN (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.91 Hz, 2H), 7.72 (m, 2H), 6.98 (d, *J* = 8.94 Hz, 2H), 6.90 (d, *J* = 9.26 Hz, 1H), 4.05 (m, 4H), 2.30 (s, 3H), 1.83 (m, 4H), 1.49 (m, 4H), 1.34 (m, 40H), 0.90 (m, 6H), (**Figure S26**).

Table S1. Transition temperatures between the crystalline (Cr), Nematic (N) and isotropic liquid (IL) of the azobenzene derivatives described above. The transition temperatures were obtained by Differential Scanning Calorimetry (DSC) measurements, performed in a TA Instrument Q200 system with a TA refrigerated cooling system RCS90. All experiments were done at 10 K/min, with four consecutive cycles to ensure stability.

# C atoms	Heating	Cooling
3	Cr 111 IL	IL 78 Cr
5	Cr 56 Cr 99 IL	IL 79 Cr 55 Cr
6	Cr 41 Cr 86 IL	IL 74 Cr
8	Cr 47 Cr 56 N 71 IL	IL 71 N 48 Cr 13 Cr
10	Cr 51 Cr 59 N 74 IL	IL 71 N 44 Cr
14	Cr 24 Cr 72 IL	IL 56 Cr 18 Cr

2. UV-Vis Absorption Spectroscopy

To prove photo isomerization of the 4,4’-dialkyloxy-3-methylazobenzene compounds, we prepared a set of thin films by spin coating 20 mL of a 4% solution of the azo-derivative in chloroform on a Corning© glass (11 mm × 22 mm). The UV-Vis absorption spectra of the films were recorded with a Jasco V-630 spectrophotometer coupled to a Jasco ETC-717 temperature controller.

Figure S1a shows the UV-Vis absorption spectra of a 4,4’-didecyloxy-3-methylazobenzene thin film, before and after illumination with UV light, at 20 ºC. As it has been previously reported in the literature[1], UV illumination induces the appearance of an absorption band at 450 nm, corresponding to the cis-isomer. The intensity of this band reduces considerably, almost disappearing, at high temperature, due to the thermal cis-trans conversion; **Figure S1c**.

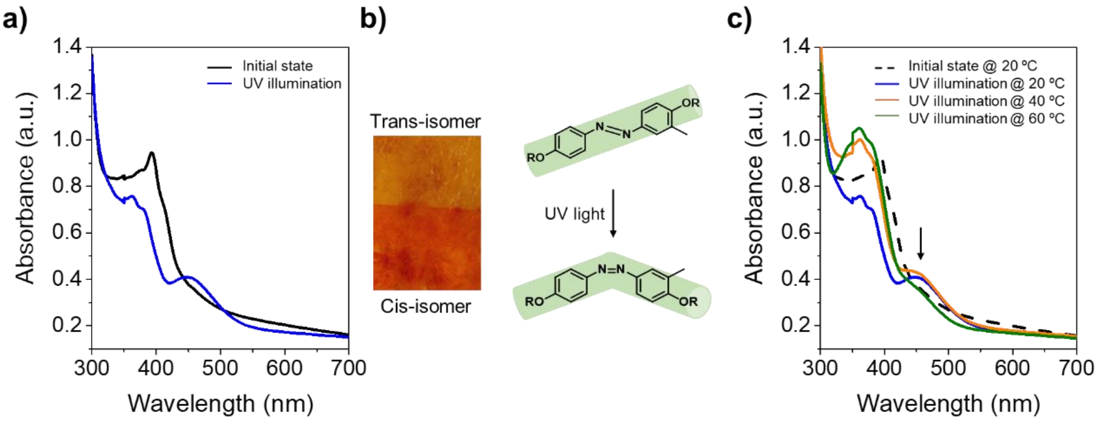


Figure S1. a) UV-Vis absorption spectra of a 4,4’-didecyloxy-3-methylazobenzene thin film as deposited (black line) and after 1 h illumination with UV light (blue line). b) Optical microscopy photograph of a thin film whose upper half was covered during UV illumination; the trans-cis isomerization is accompanied by a notable color change. c) UV-Vis absorption spectra of a 4,4’-didecyloxy-3-methylazobenzene after the UV illumination, and heating at different temperatures, to study the effect of temperature on the cis-trans isomerization.

3. Polarized Optical Microscopy

Polarized Optical Microscopy (POM) images were taken using a Leica DM2700-M microscope coupled to a Linkam stage and a LNP96-S liquid nitrogen pump, for a precise temperature control. All experiments were performed between room temperature and the melting temperature of each compound at 2 K/min, to study their concordance with the DSC scans. **Figures S2-S6** show the temperature cycles for 4,4’-dialkyloxy-3-methylazobenzenes with n=6, 8 and 10; the liquid crystal 8CB and the 8CB:azobenzene dispersion.

Figure S2. Polarized optical microscopy images of the heating-cooling cycles of 4,4’-dihexyloxy-3-methylazobenzene, observing a complete transition from a crystalline solid to an isotropic liquid on heating above 367 K.

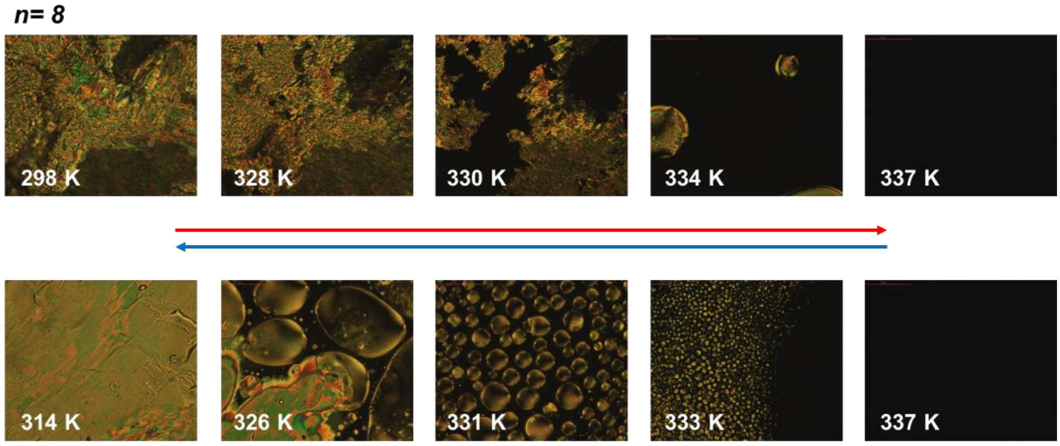


Figure S3. Polarized optical microscopy images of the heating-cooling cycles of 4,4'-dioctyloxy-3-methylazobenzene, observing a transition (on heating) from a crystalline solid to a liquid crystal (328 K) before melting into an isotropic liquid (337 K).

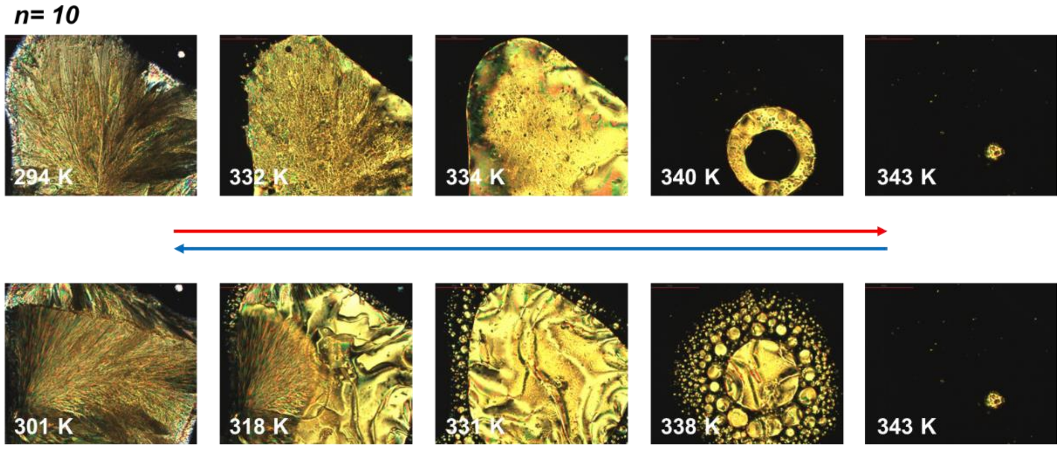


Figure S4. Polarized optical microscopy images of the heating-cooling cycles of 4,4'-didecyloxy-3-methylazobenzene, observing a transition (on heating) from a crystalline solid to a liquid crystal (334 K) before melting into an isotropic liquid (340 K).

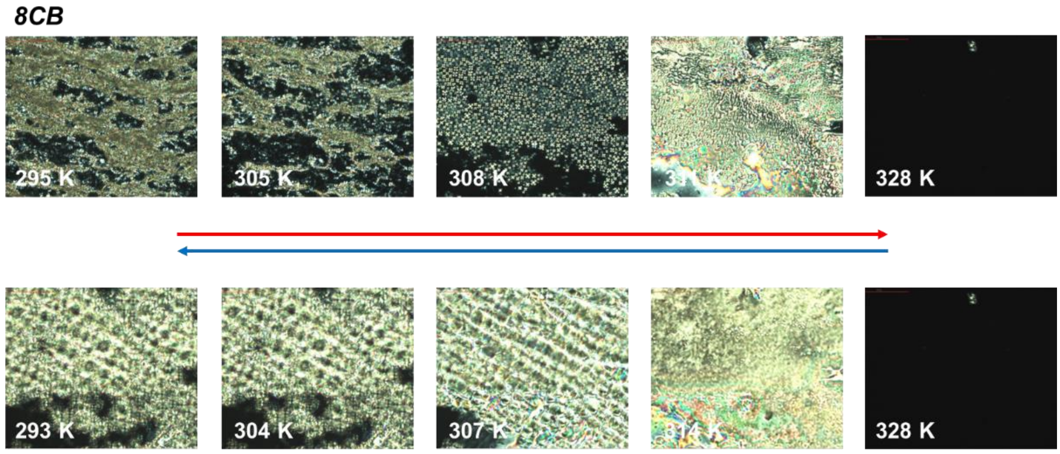


Figure S5. Polarized optical microscopy images of the heating-cooling cycles of 4-octyl-4'-cianobiphenil (8CB), which forms a smectic A liquid crystal mesophase at room temperature (295 K), and then stabilizes a nematic liquid crystal (308 K) before melting into the isotropic liquid phase (315 K).

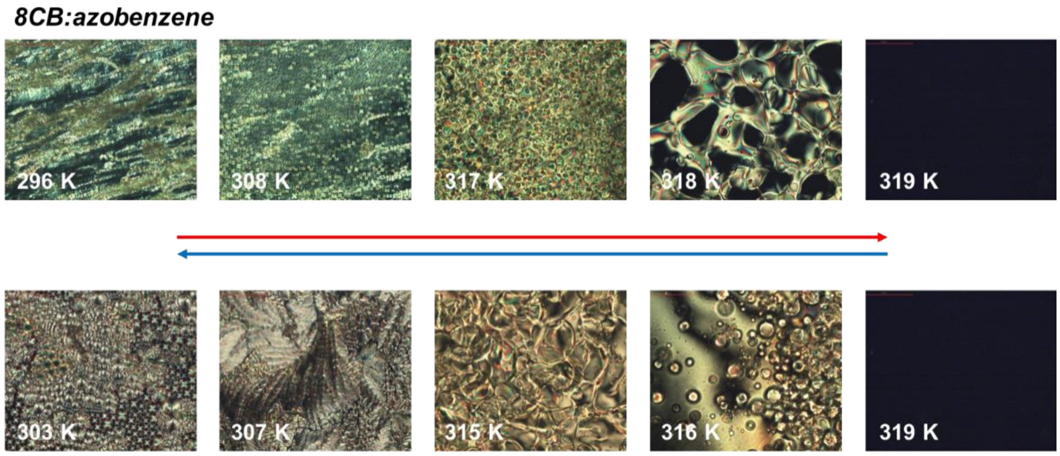


Figure S6. Polarized optical microscopy images of the heating-cooling cycles of the 8CB:azobenzene dispersion. The system behaves like pure 8CB.

To check the trans-cis photoisomerization, POM images were recorded while illuminating the azobenzene derivatives (n=6, 8 and 10) with UV light (365 nm) (**Figures S7-S9**).

Figure S7. Polarized optical microscopy images of 4,4'-dihexyloxy-3-methylazobenzene while being illuminated with UV light for 18 min at 313 K. Tran-cis isomerization results into a crystal-to-liquid transition.

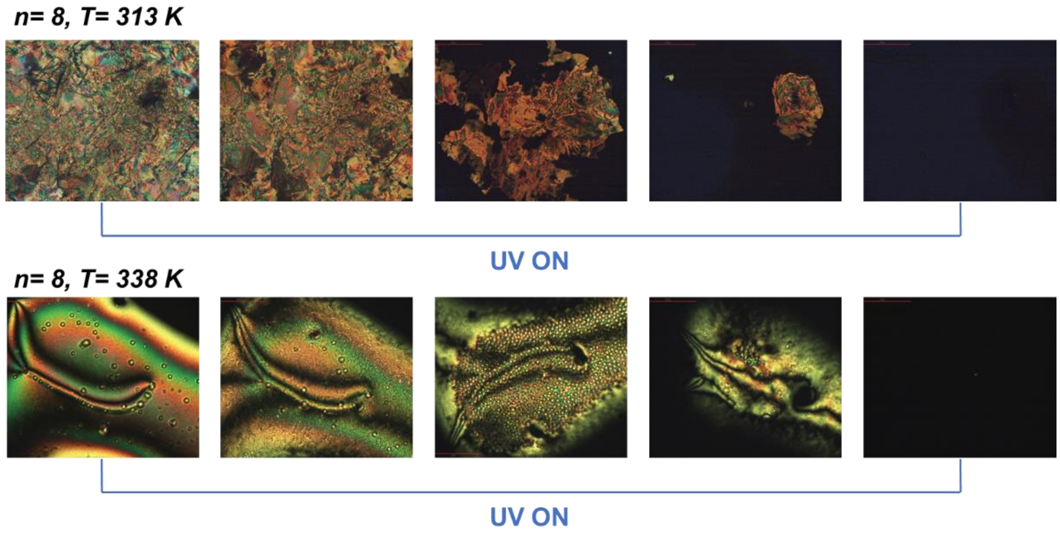


Figure S8. Polarized optical microscopy images of 4,4'-dioctyloxy-3-methylazobenzene while being illuminated with UV light during 9 min at 313 K (top panel) resulting in the crystal to isotropic liquid transition, and at 338 K for 30 s (bottom panel) showing the liquid crystal to isotropic liquid transition.

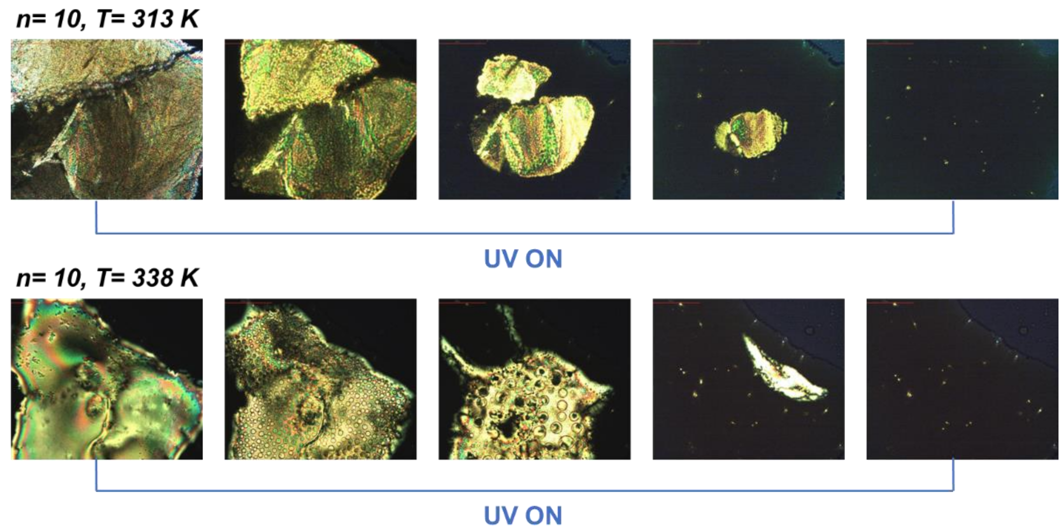


Figure S9. Polarized optical microscopy images of 4,4'-didecyloxy-3-methylazobenzene during UV illumination at 313 K for 19 min (top panel), showing the crystal to isotropic liquid transition, and at 338 K for 26 s (bottom panel), showing the liquid crystal to isotropic liquid transition.

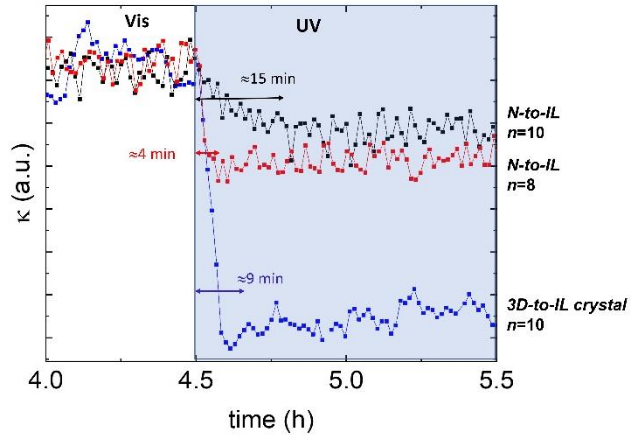


Figure S10. Time-dependence of the thermal conductivity during transition towards the IL phase upon UV illumination. The figure shows the traces for the transition from the 3D crystal in n=10, and the N-LC in n=10 and n=8 to the IL.

4. Thermal Conductivity Measurements

Thermal conductivity measurements were performed in a liquid nitrogen cryostat using the 3ω method in a homemade setup [2]. The heater/sensor was a Pt resistance (1 mm long, 10 μm wide, 100 nm thick) deposited by optical lithography on a low thermal conductivity glass (**Figure S11a**). For the measurements, we melted a small amount of the sample ($\approx$100 μg) on top of the platinum resistance (**Figure S11b**); thermal conductivity was measured during thermal scan rates at 1 K/min from the 3ω voltage at 76 and 362 Hz (linearity of 3ω vs $\ln(2\omega)$ was verified between 10 Hz and $\approx$500 Hz).

Isothermal illumination cycles were performed using two LED lights (365 and 445 nm) incorporated inside the cryostat. Liquid nitrogen was used to minimize any possible self-heating of the LEDs.

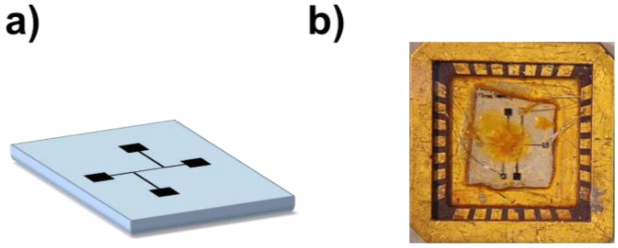


Figure S11. a) Schematic representation of the platinum resistance deposited on top of a cover glass. b) Optical microscopy photograph of the experimental setup used to measure thermal conductivity with the 3ω method. A small amount of an azobenzene-derivative is deposited on top of the Pt sensor.

To record the temperature rise during the LED illumination, we used the calibrated dR/dT of the Pt sensor of the 3ω setup (**Figure S12a**). As shown in **Figure S12b**, the change in R during UV illumination at the maximum power used produces a maximum temperature rise of 2.5 K.

To avoid any possible thermal effect, the illumination cycles of the azobenzene derivatives were performed at temperatures much lower than the melting temperature of the compounds. All the solid-to-liquid or liquid crystal-to-liquid transitions reported in this paper under UV light illumination are produced by trans-cis isomerization of the azobenzene core, and not due to the local increase of temperature.

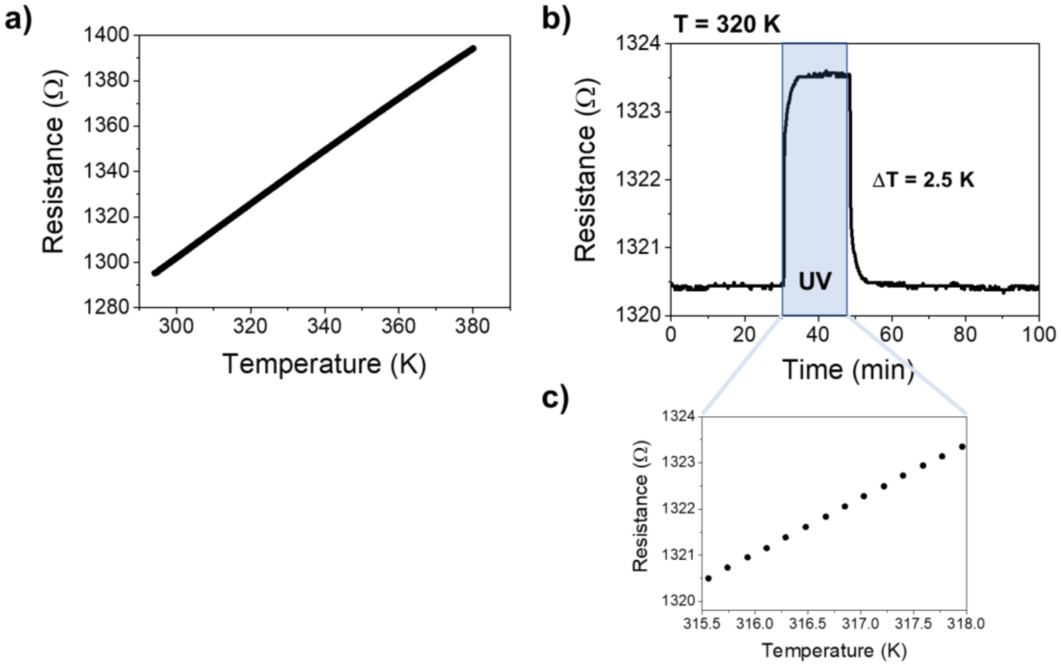


Figure S12. a,c) Resistance vs. temperature dependence of the Pt resistor. b) Measurement of the platinum resistance during ultraviolet illumination. dR/dT calibration demonstrates that UV irradiation induces a maximum temperature rise of 2.5 K.

5. Characterization of the 8CB Liquid Crystal

Figure S13 shows the DSC scans of the pure liquid crystal 4-octyl-4'-cianobiphenil (8CB) and a 4% (w/w) dispersion of 4,4'-dihexyloxy-3-methylazobenzene in 8CB (8CB:azobenzene). Both thermal scans are almost identical, showing that the presence of the azobenzene does not affect the stability of the different phases of 8CB.

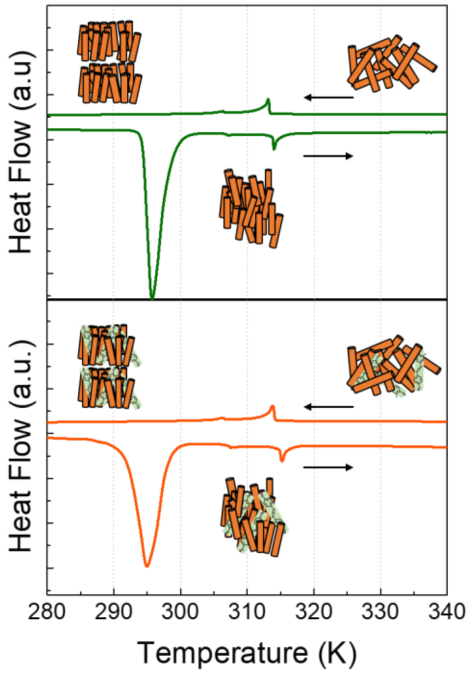


Figure S13. Differential scanning calorimetry of 4-octyl-4'-cianobiphenil (8CB) liquid crystal (top panel), and the same liquid crystal doped with a 4% (w/w) of 4,4'-dihexyloxy-3-methylazobenze (bottom panel).

To determine if 4-octyl-4'-cianobiphenil (8CB) was a suitable candidate to act as a LC matrix for our azobenzene dispersions, we first quantified the thermal contrast between its different phases (**Figure S14a),** obtaining a ≈20% decrease in thermal conductivity for the Sm-L transition. In addition to this, we also checked the behavior of this LC under UV/Vis illumination, obtaining no change in thermal conductivity **Figure S14 b)**. This means that the thermal conductivity change observed in the 8CB:azobenzene dispersion is only due to the trans-cis isomerization of the azobenzene dopant molecules.

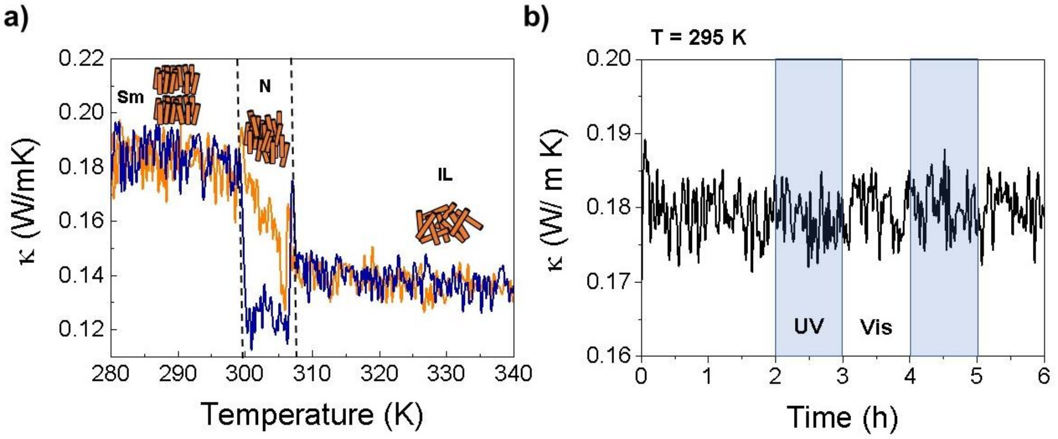


Figure S14. Thermal conductivity measurements of pure 4-octyl-4'-cianobiphenil (8CB) with temperature (a) and during UV/Vis cycles at 295 K (b). 8CB does not absorb the light wavelengths used in this study (365 and 445 nm), so there is no change in thermal conductivity when irradiated.

The effect of UV-Vis illumination on the structure of pure 8CB liquid crystal was also studied with POM. The results show no change at all during illumination, (**Figure S15**, top panel), ruling out also any possible effect of temperature (light-heating).
However, when a small amount of 4,4'-dihexyloxy-3-metylazobenzene (4% w/w) is dispersed in the 8CB, UV illumination induces trans-cis isomerization of the azobenzene core and destabilizes the LC matrix (**Figure S15**, bottom panel). The large patches of isotropic liquid form a percolating pattern that determines the thermal transport of the whole system.

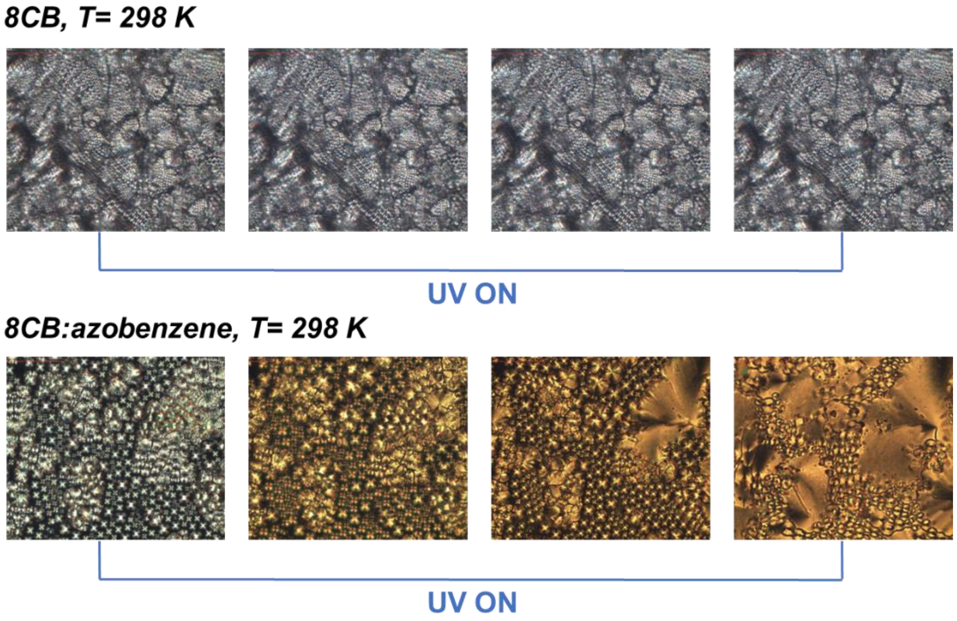


Figure S15. Polarized optical microscopy images of pure of 4-octyl-4’-cianobiphenil (8CB) (top panel) and 8CB:azobenzene dispersion (bottom panel) during UV illumination at room temperature.

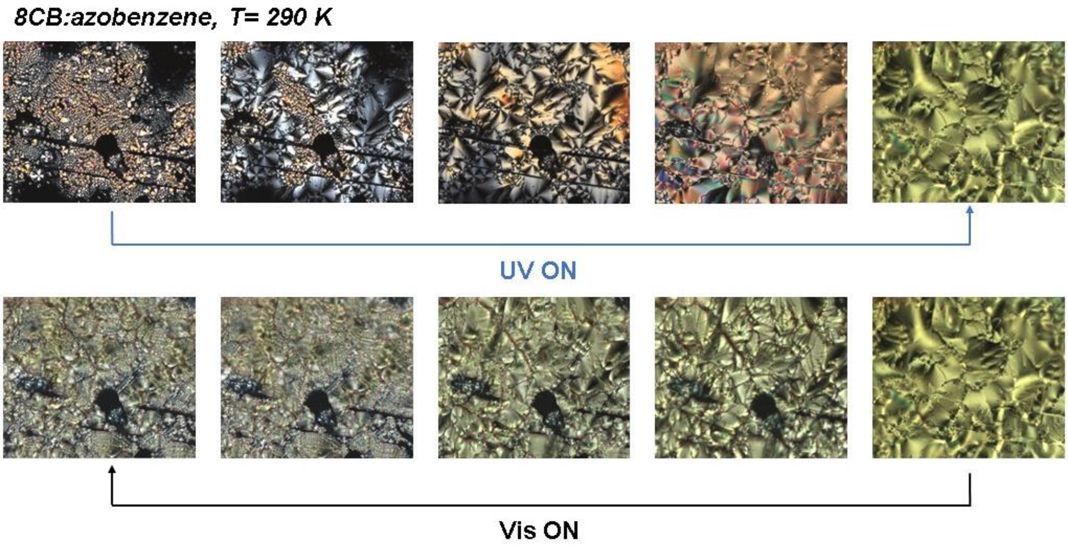


Figure S16. Polarized optical microscopy images of the 8CB:azobenzene dispersion under UV illumination (total time 18 min) and Visible light (55 minutes), at 290 K, when the liquid crystal is in the Sm-phase.

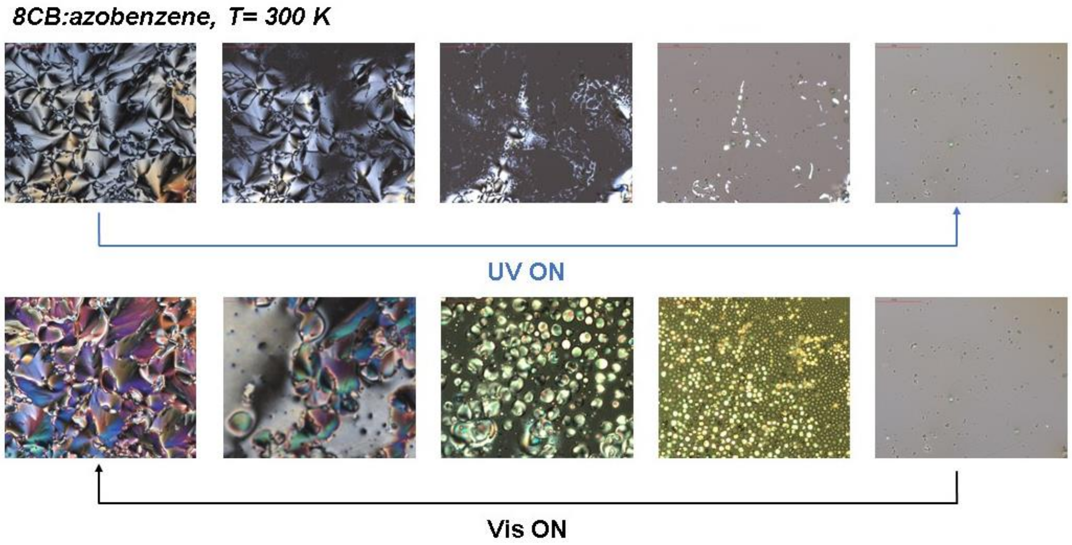


Figure S17. Polarized optical microscopy images of the 8CB:azobenzene dispersion under UV illumination (total time 1 min) and Visible light (1 minute), at 300 K, when the liquid crystal is in the N-phase.

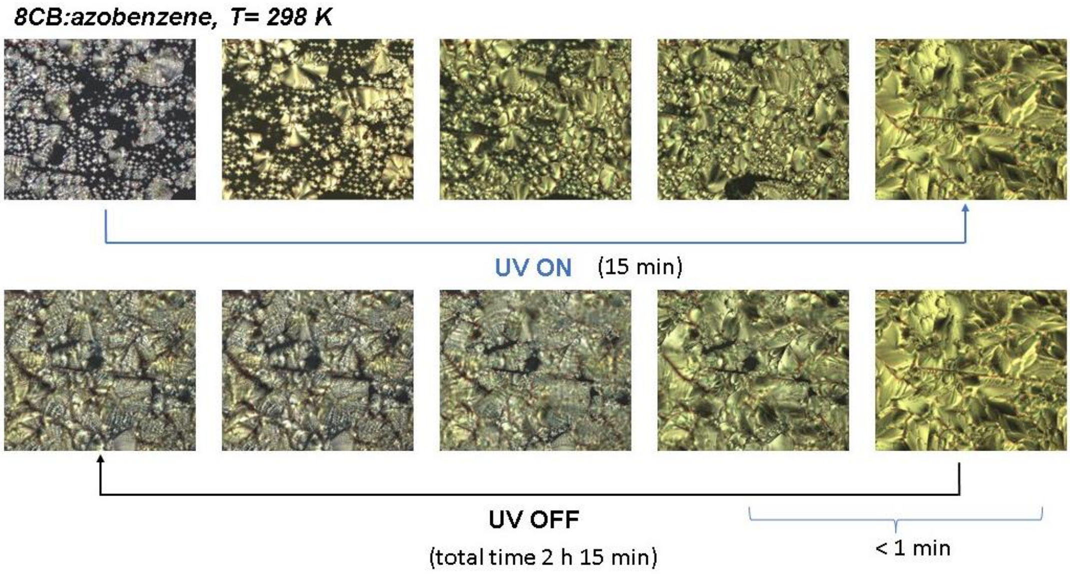


Figure S18. Polarized optical microscopy images of the 8CB:azobenzene dispersion under UV illumination (total time 15 min) and under dark. After switching off the UV light, the system transits very rapidly, in less than a minute, to an intermediate phase, before slowly relaxing back to the Sm-phase.

6. ^{1}H-NMR Spectra

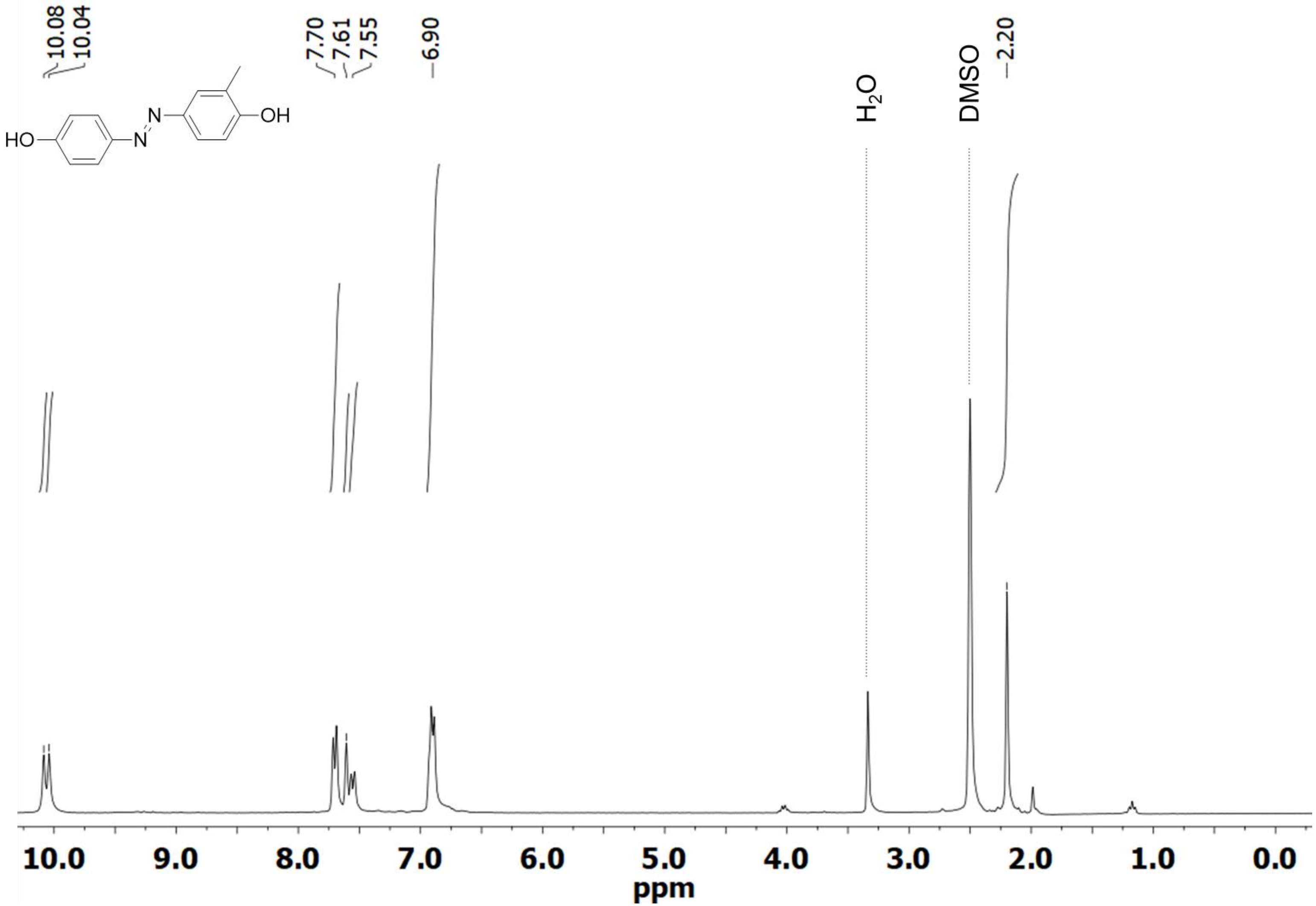


Figure S19. ^{1}H-NMR spectrum of 4,4’-dihydroxy-3-methylazobenzene.

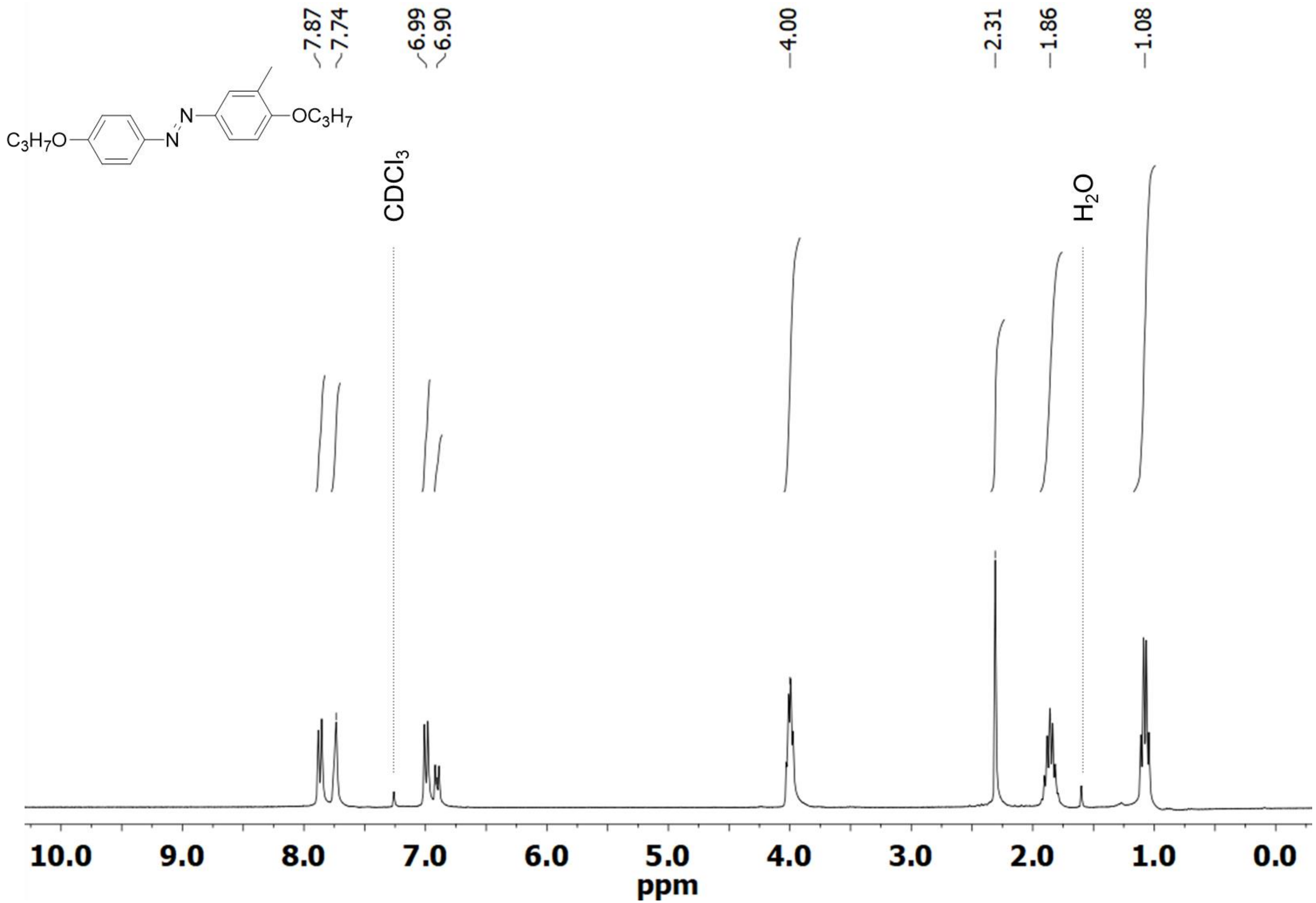


Figure S20. ^{1}H-NMR spectrum of 4,4'-dipropyloxy-3-methylazobenzene.

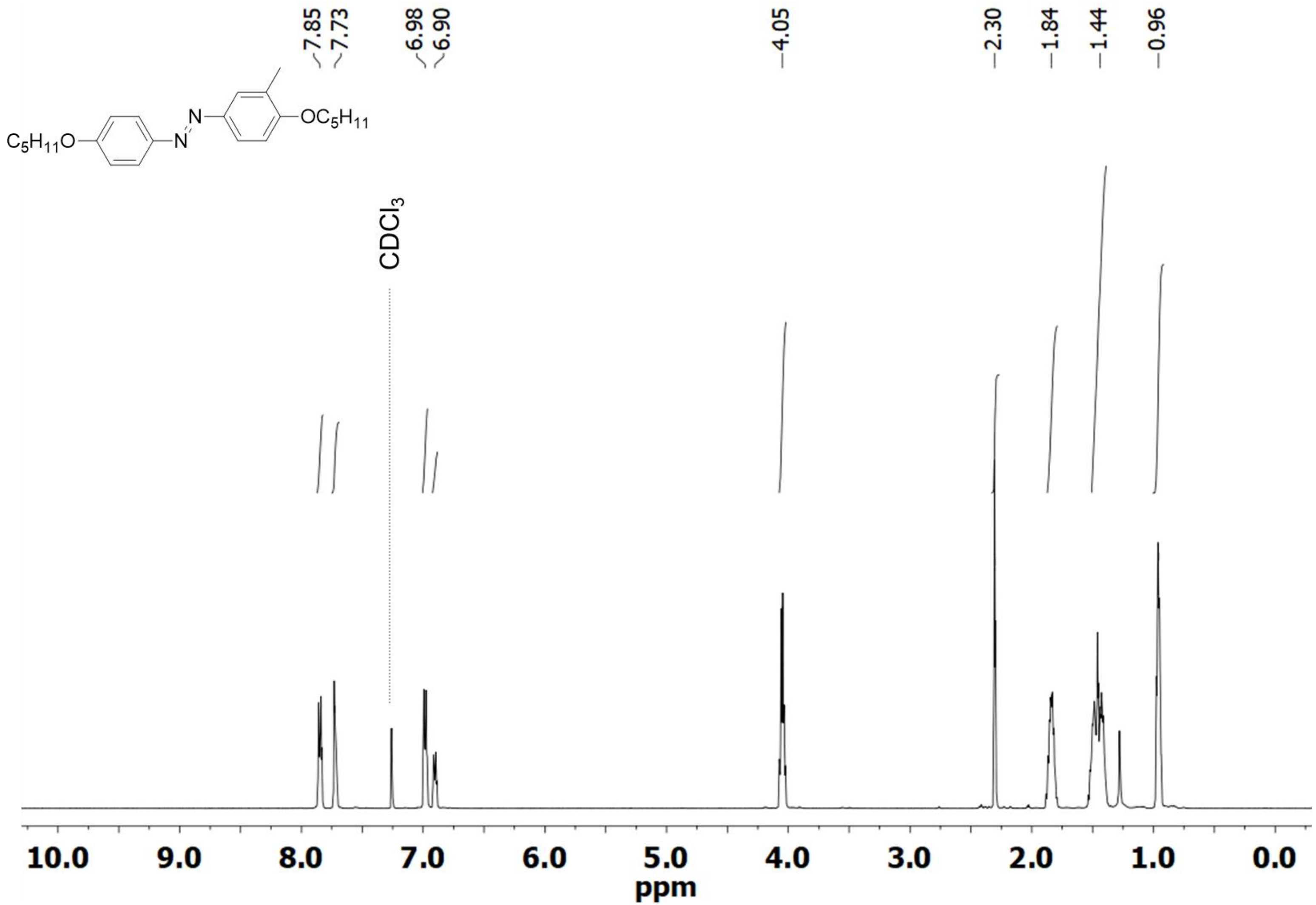


Figure S21. ^{1}H-NMR spectrum of 4,4'-dipentyloxy-3-methylazobenzene performed at 328 K.

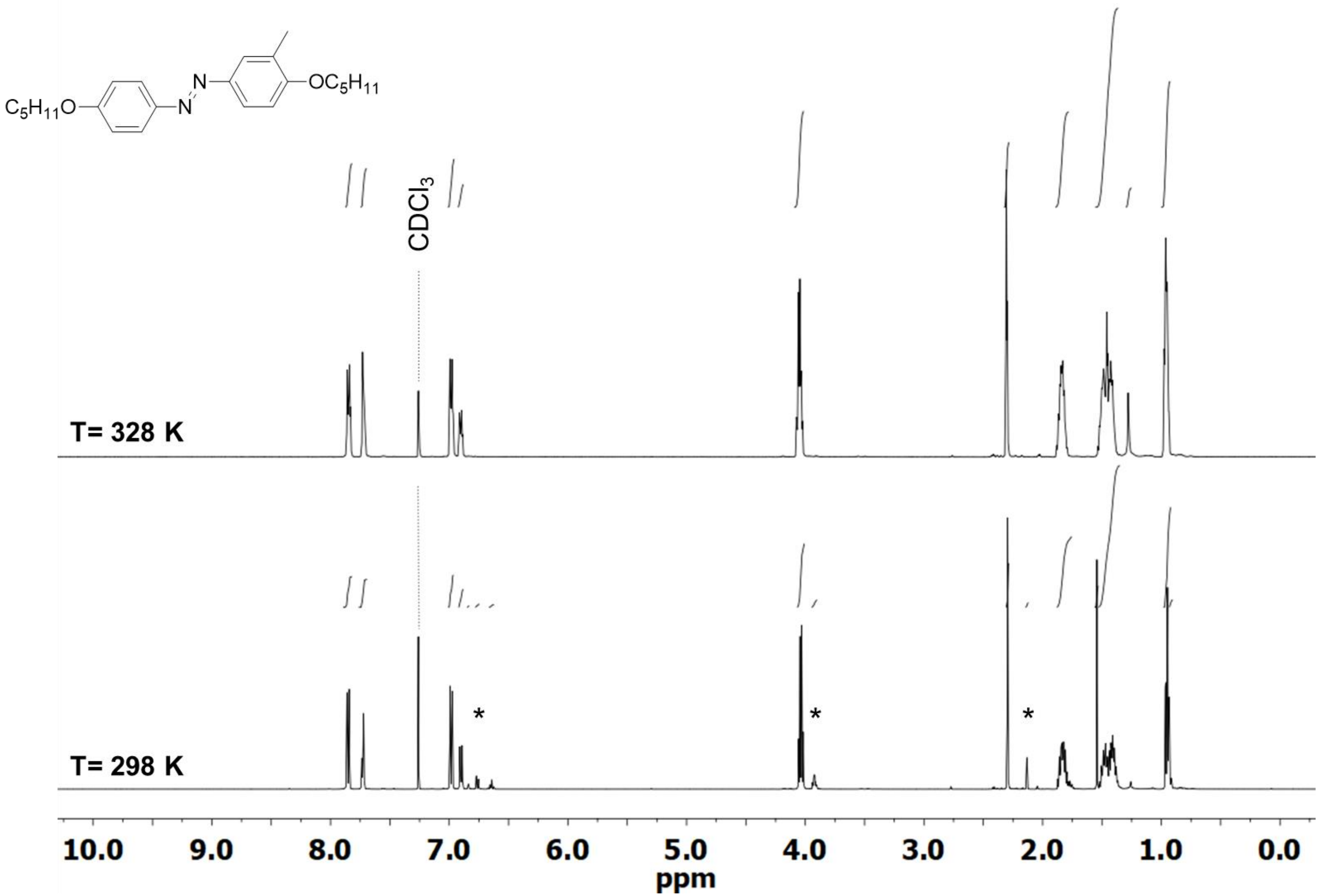


Figure S22. Comparison between the ^{1}H-NMR spectra of 4,4-dipentyloxy-3-methylazobenzene performed at 298 and 328 K. Signals marked with and asterisk correspond to the cis isomer.

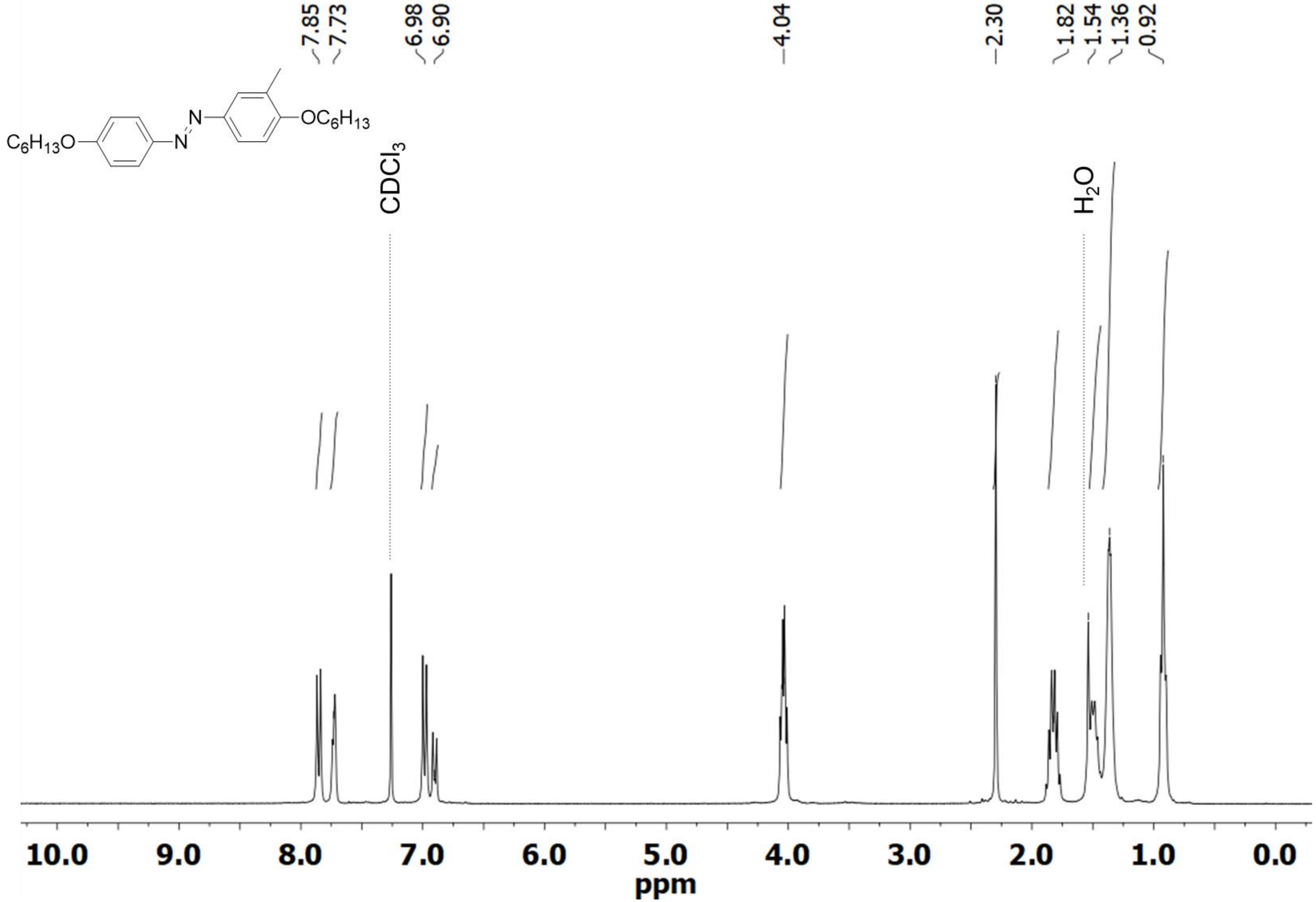


Figure S23. ^{1}H-NMR spectrum of 4,4’-dihexyloxy-3-methylazobenzene.

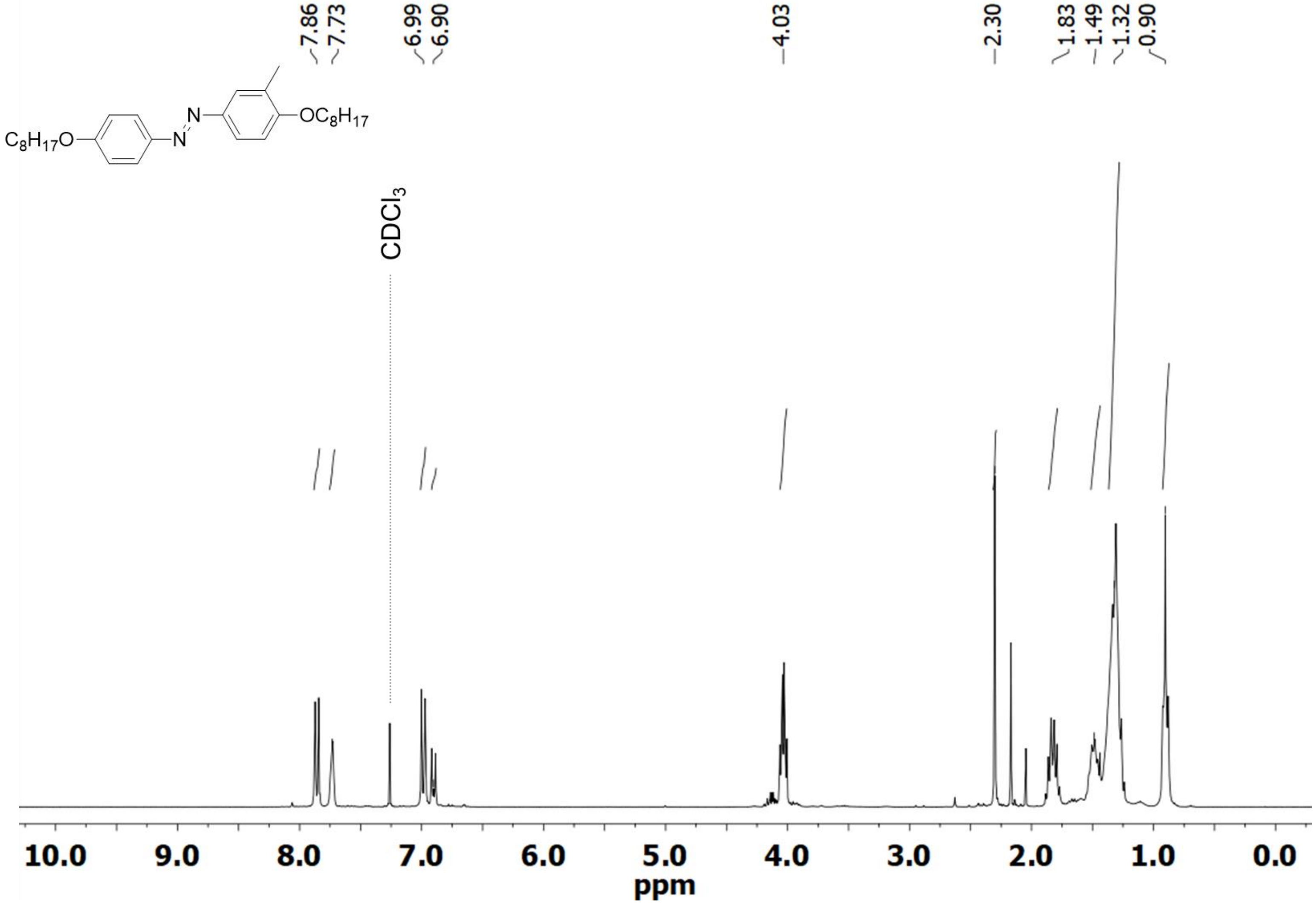


Figure S24. ^{1}H-NMR spectrum of 4,4'-dioctyloxy-3-methylazobenzene.

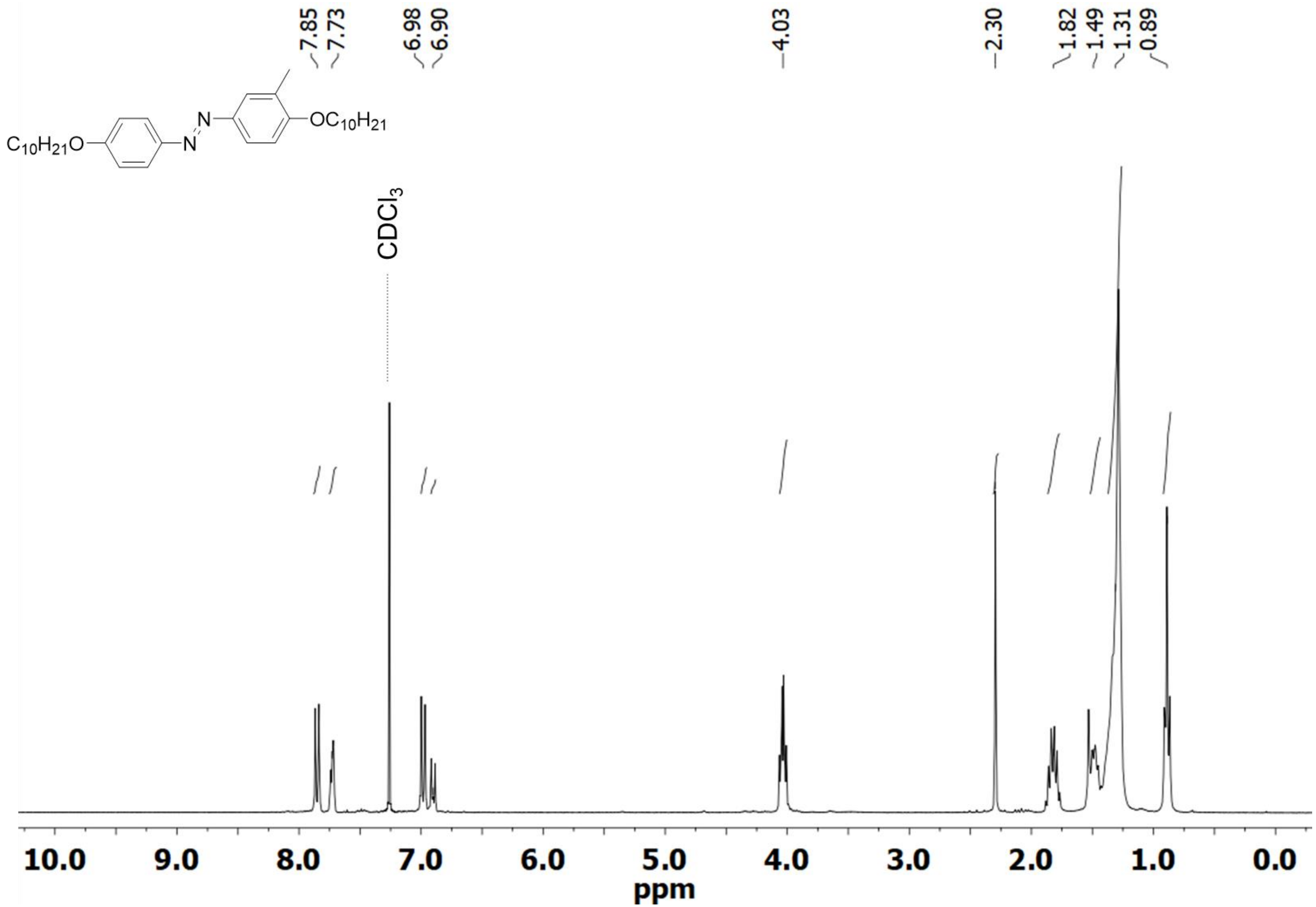


Figure S25. ^{1}H-NMR spectrum of 4,4'-didecyloxy-3-methylazobenzene.

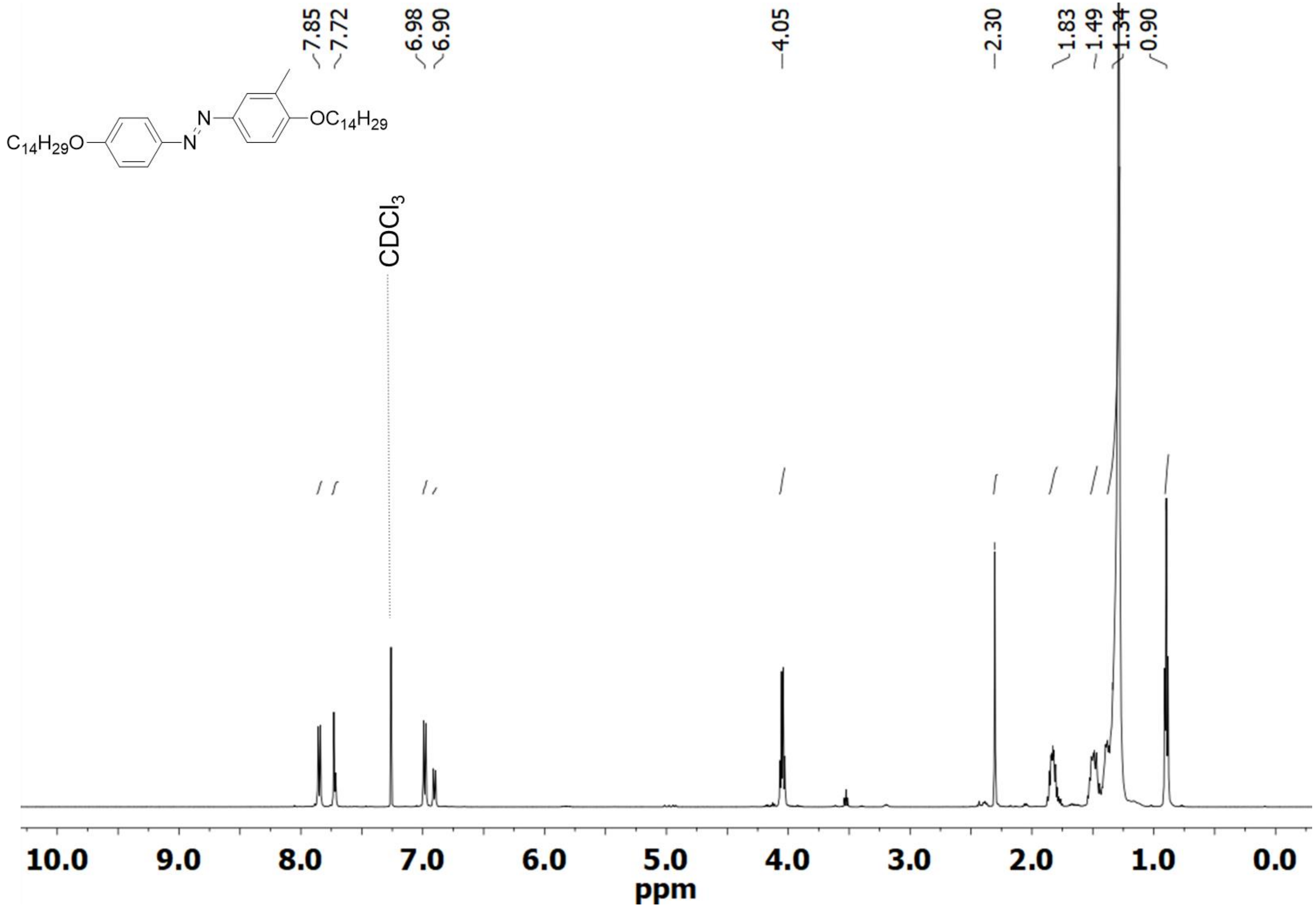


Figure S26. ^{1}H-NMR spectrum of 4,4'-ditetradecyloxy-3-methylazobenzene.

References

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