Electronic Supplementary Information

- New Journal of Chemistry -

PHOTOISOMERIZABLE AZOBENZENE STAR-SHAPED LIQUID CRYSTALS: BYPASSING THE ABSENCE OF HYDROGEN BONDING

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Content

1. METHODS

1.1. Characterizations

All ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker 200DPX spectrometer, operated at 4.7 Tesla, operating at 200 MHz and 50 MHz, respectively. The deuterated solvents used were chloroform ($CDCl_3$) and dimethyl sulfoxide (DMSO-d_6), both containing tetramethylsilane (TMS) as an internal standard. The HRMS analyzes were performed in a micrOTOF-Q (Bruker) equipment with atmospheric pressure chemical ionization (APIC, from Atmospheric Pressure Chemical Ionization).

1.2. Thermal analysis

DSC thermograms were obtained on a TA Instruments Q2000 calorimeter equipped with an RCS90 cooling module. Heating/cooling rates of 10 $^{o}C \cdot min^{-1}$ and a nitrogen flow of 50 $mL \cdot min^{-1}$ were used. Decomposition temperatures were determined on a Shimadzu instrument equipped with a TGA-50 module. Heating rates of 10 $^{o}C \cdot min^{-1}$ and a nitrogen flow of 50 $mL \cdot min^{-1}$ were used. Melting points, transition temperatures, texture observation and photo acquisition were determined on an Olympus BX53 microscope equipped with a Mettler Toledo FP-82 Hot Stage and Olympus DP73 digital camera.

1.3. X-Ray diffraction

XRD measurements were performed with an X'Pert PRO (PANalytical) diffractometer using a Cu Kα radiation (λ = 1.5418 Å). Films were prepared by depositing a small amount of the compound on a glass plate, heating to the isotropic liquid and cooling to the desired temperature. During the analysis, temperature was controlled with a TCU2000 – Temperature Control Unit (Anton Paar). The scans were performed in continuous mode from 2° to 30° (2Θ angle) and the diffracted radiation collected with an the X'Celerator detector.

1.4. Photochemistry analysis

The photoisomerization experiments were performed in a UV-Vis Varian Carey spectrophotometer. All target compounds were solubilized in chloroform resulting 10^{-5} $mol \cdot L^{-1}$. The freshly prepared solution was heated to favor the predominance of the E isomer, and placed under analysis, obtaining the absorbance spectrum in the region between 250 nm and 550 nm. Subsequently, the cuvette containing the solution was irradiated by a UV-lamp (365 nm) from 1 to 5 minutes, in a closed box, so that the interference from ambient light is avoided, and the absorbance spectrum was measured again. Finally, to investigate the reverse photoisomerization, the cuvette was exposed to a 310 nm light source from 1 to 5 minutes, and its absorption spectrum

was then recorded. Similar photoisomerization experiment was performed using the Bruker 200DPX NMR equipment. After measuring the ^{1}H NMR spectrum **OXA-L,** the sample containing only the E isomer was subjected to 365 nm light exposure for 10 to 30 minutes. After this period of exposition, a new ^{1}H NMR spectrum was recorded.

Photoisomerization measurement in the Colh were performed using a Olympus BX53 microscope equipped with a Mettler Toledo FP-82 Hot Stage controlled heating plate and Olympus DP73 digital camera, and a commercial 405 nm laser pointer (5 mW). The sample was taken to the isotropic liquid using the POM hot-stage, and cooled to a few degrees below to Iso-Col$_h$ transition. The temperature was maintained until stabilization of the texture formed. At this moment, the laser beam was focused on the sample surface through the hot-stage slit, without opening the oven or changing the sample temperature. After all texture vanished, the laser was turned off and the temperature of the sample was maintained constant until the complete return of texture.

2. ADDITIONAL DATA FOR THERMAL ANALYSIS

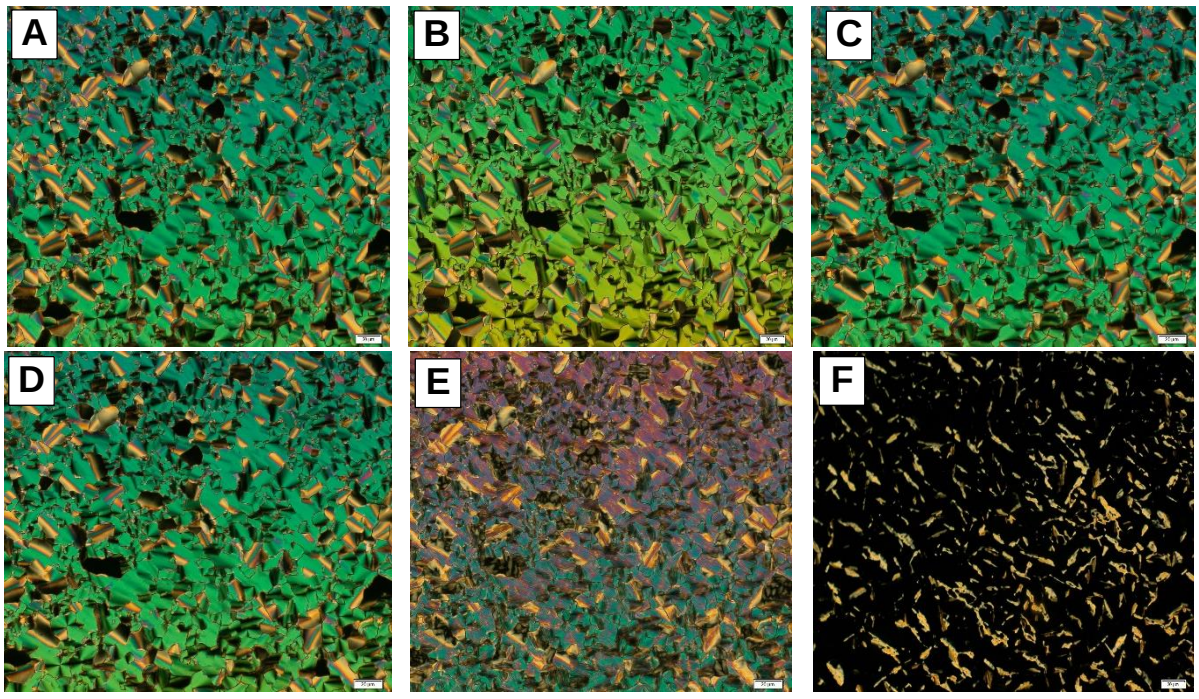


Figure S1 - **EST-Bn** under cooling and heating. **A**, **B** and **C**: Cooling, at 90 ºC, 70 ºC and 40 ºC, respectively, showing no changes in the textures, just in the birefringence. **D**, **E** and **F**: under heating, at 70 ºC, 80 ºC and 120 ºC, respectively.

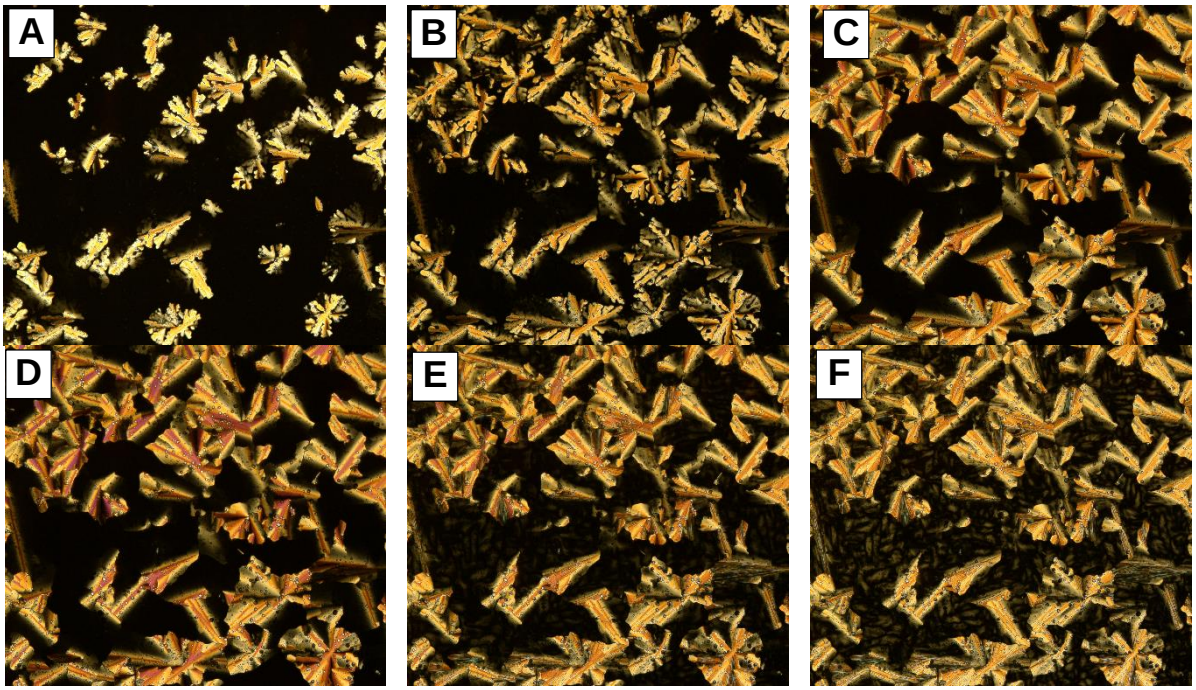


Figure S2 – Textures for AMD-Bn on the same sample region. **A - D**: Cooling, at 128.0 ºC, 127.8 ºC, 110.0 ºC and 77.0 ºC, respectively. **E** and **F**: under heating, at 89.5 ºC and 120.0 ºC, respectively, showing the appearance of a texture on the regions of homeotropic alignment.

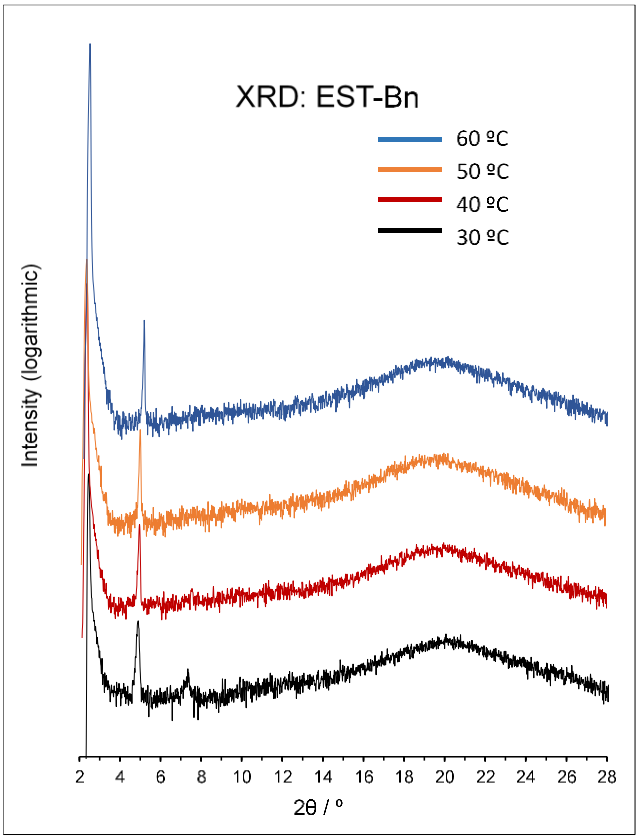


Figure S3 – XRD of EST-Bn during cooling at four different temperatures, with absence of crystallization even at room temperature.

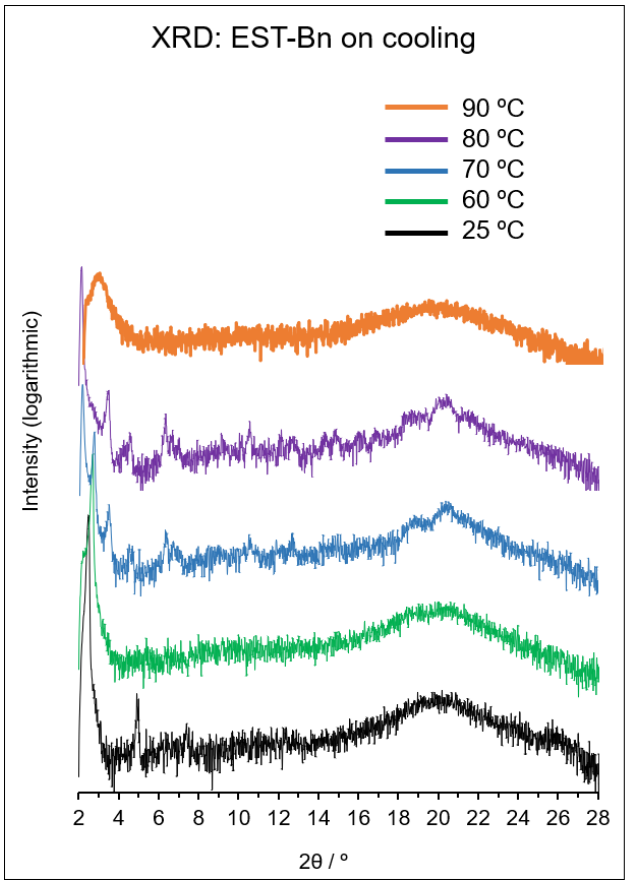


Figure S4 – XRD of EST-Bn on heating from room temperature (25 °C) to the isotropic liquid (90 °C), showing the crystallization around 70 °C.

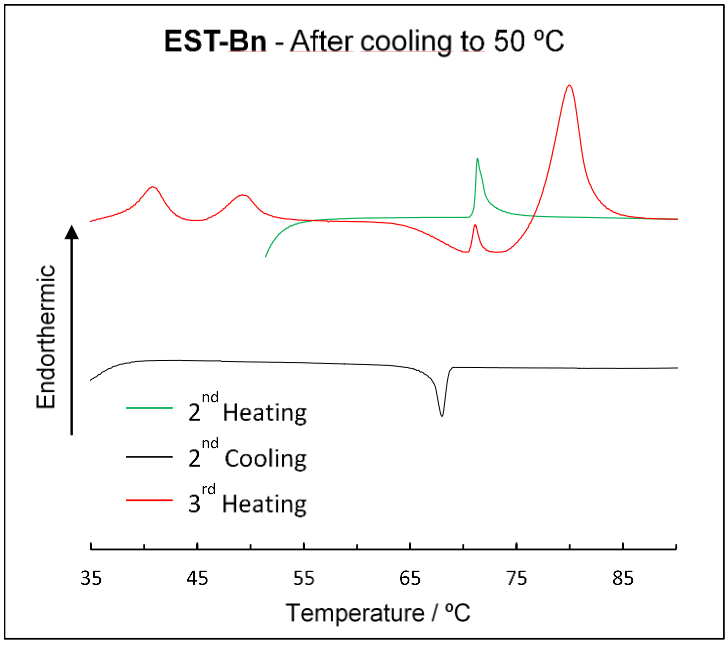
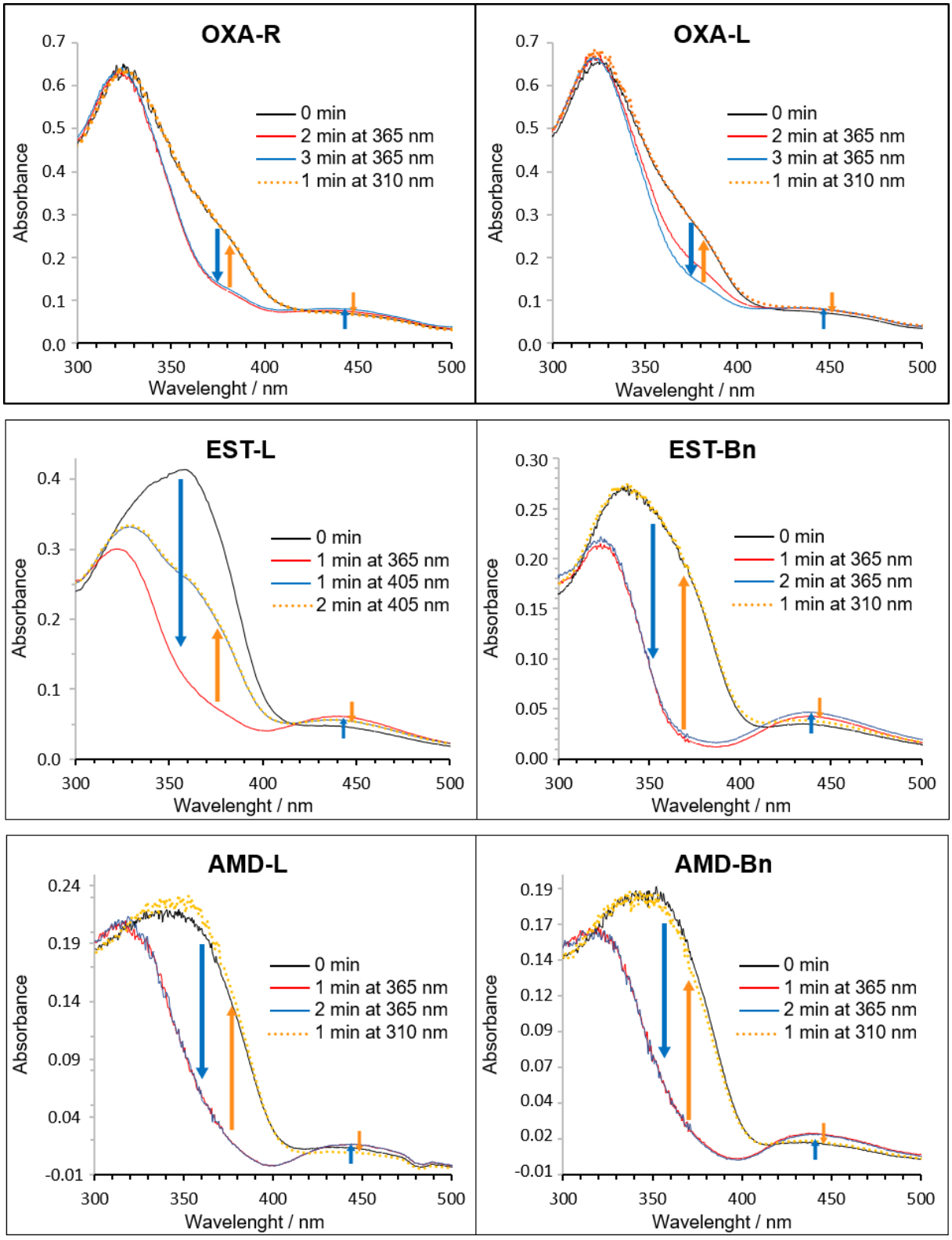


Figure S5 - DSC curve of **EST-Bn**, after it was heated to 100 ºC and cooled to 50 ºC. After that, it was heated again to 100 ºC (green, 2nd Heating), cooled to 30 ºC (black, 2nd Cooling) and heated one last time to 100 ºC (red, 3rd Heating).

3. ADDITIONAL DATA FOR PHOTOCHEMISTRY ANALYSIS



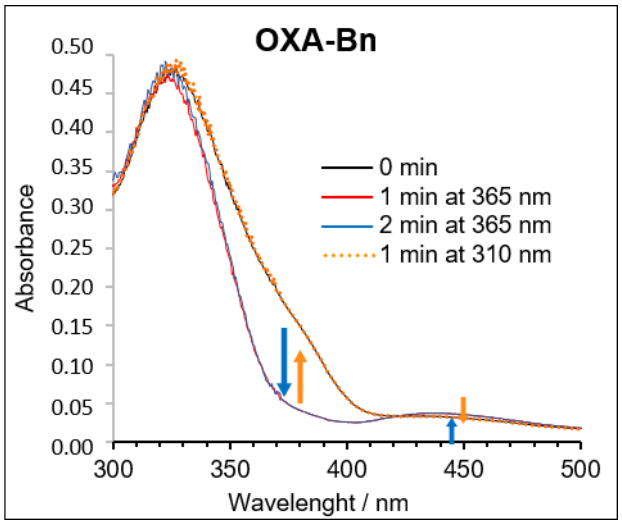


Figure S6 (continuation) - UV-Vis measurements for all seven azocompounds in solutions of 10^{-5} mol.L^{-1}. After the solutions have been irradiated by a 365 nm lamp, they were irradiated by a 310 nm lamp, or by a 405 nm lamp, in case of **EST-L**. Such irradiations took place in a closed vat with a dark coating, so that they were protected from ambient light. The blue arrows indicate what happens to the *Z* and *E* bands, whether the intensities are increased (arrow pointing up) or decreased (arrow pointing down), during the *E* to *Z* interconversion. Orange arrows indicate the opposite, *i.e.*, the interconversion from *Z* to *E*.

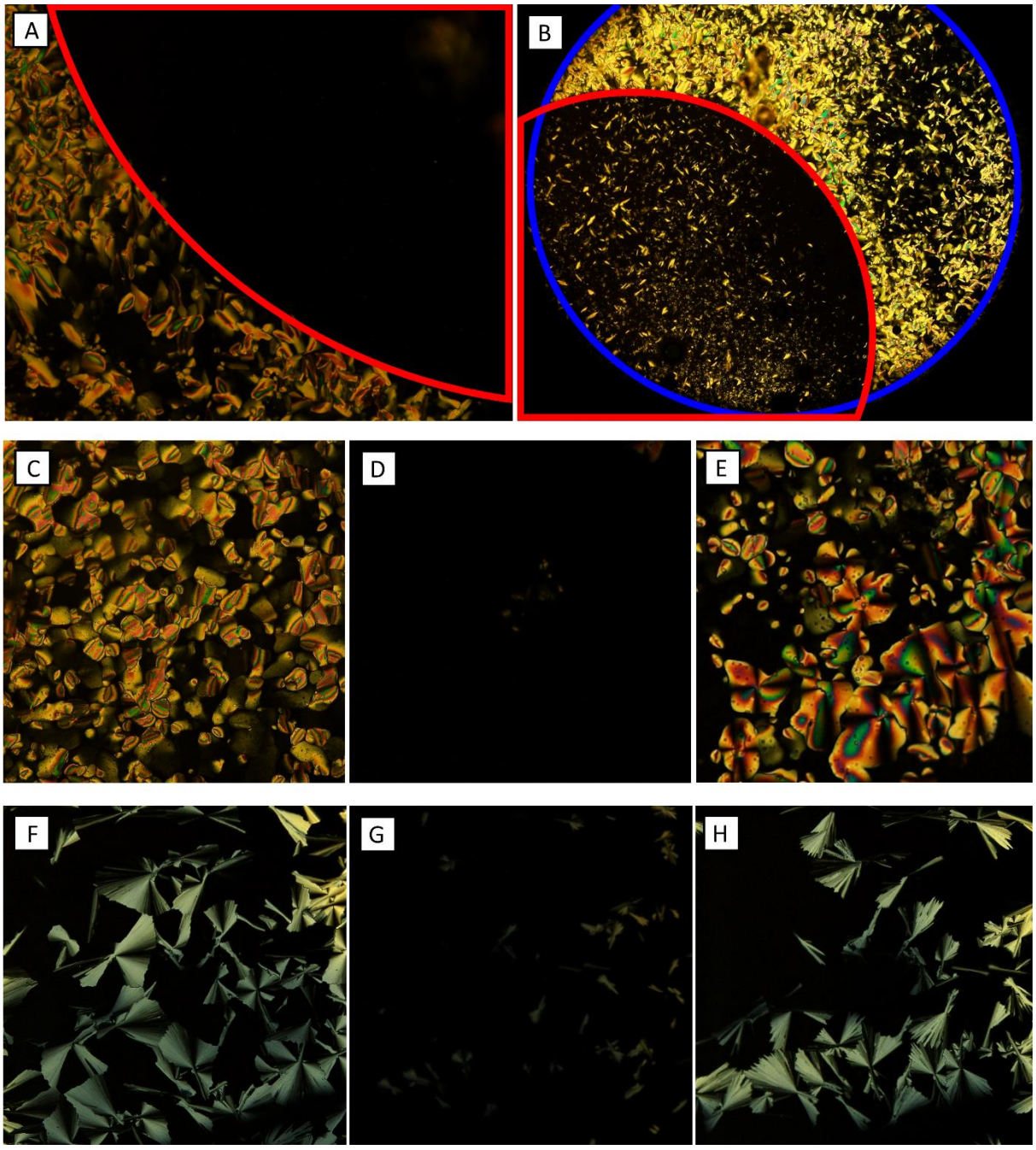
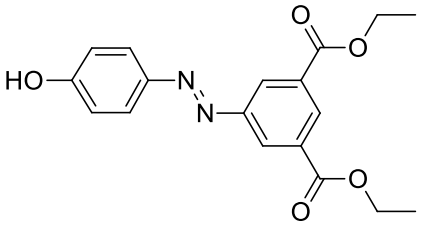


Figure S7 – Photoisomerization analysis on the Col_h mesophase promoted by a 405 nm laser beam (5 mW), showing the disruption of the columnar packaging due the texture disappearance and its thermal regeneration:
• **EST-Bn** at 65 ºC: **A)** After 3 minutes of irradiation (red: Laser affected area); **B)** After 5 minutes of laser shutdown (blue: Region observed by the microscope lens - with lower magnification);
• **OXA-Bn** at 119 ºC: **C)** Before the irradiation; **D)** After 5 minutes of irradiation; **E)** After 5 minutes of laser shutdown;
• **AMD-Bn** at 127 ºC: **C)** Before the irradiation; **D)** After 3 minutes of irradiation; **E)** After 5 minutes of laser shutdown.

4. SYNTHESIS

All organic and inorganic reagent and solvents were of the highest purity, purchased from commercial sources (Merck, Sigma-Aldrich, Fluka, Vetec and Acros Organics), and used as received. Compound 1,2-bis(dodecyloxy)-4-nitrobenzene was already available and was synthesized according to reference 1. Dichloromethane, dimethylformamide and pyridine were dried using molecular sieves 3Å during 24 hours. Purifications were carried out by recrystallization using commercial grade solvents and by column chromatography on silica-gel 60–200 mesh 60A (Merck). Thin layer chromatography (TLC) was performed on aluminum sheets pre-coated with silica gel (Merck, Si 60-F254).

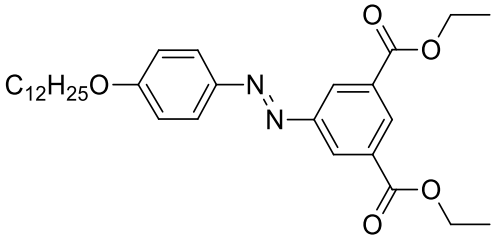
Diethyl (*E*)-5-(4-hydroxyphenyl)diazenyl isophthalate (3)



A solution of diethyl 5-aminoisophthalate (**1**) (1.02 g, 4.30 mmol) in distillated water (10 mL) was stirred in a 50 mL beaker and cooled to near 0 ºC using an ice bath. To the mixture concentrated HCl (2.5 mL) was slowly added. Then, a 1.5 $mol.L^{-1}$ aqueous solution of $NaNO_2$ (3 mL, 4.63 mmol) was added dropwise for 15 minutes and the resulting mixture was maintained under stirring for further 30 minutes. This solution containing the diazonium salt was directly used for the synthesis of diazenil by means of azo coupling, as described below.

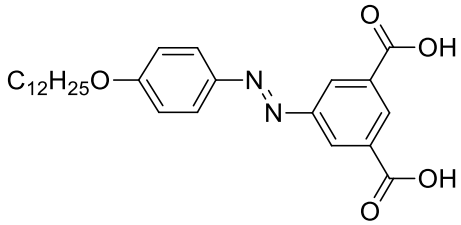
A 50 mL beaker containing phenol (0.50 g, 5.32 mmol), K_2CO_3 (1.29 g, 9,35 mmol) and distilled water (15 mL) was stirred in an ice bath. To this, the diazonium salt solution was slowly added (15 minutes). During the addition, it was possible to notice the appearance of an intense orange color. After two hours of reaction, the ice bath was removed and concentrated HCl was added until pH ≈ 3. The precipitate was filtered and recrystallized in EtOH/H_2O, yielding 45% of an intense orange solid. **^{1}H NMR** ($CDCl_3$) δ ppm: 1.46 (t, *J* = 7.1 Hz, 6H, CH_3), 4.47 (q, *J* = 7.1 Hz, 4H, -OCH_2-), 6.99 (d, *J* = 8.9 Hz, 2H, Ar-H), 7.94 (d, *J* = 8.9 Hz, 2H, Ar-H), 8.69 (d, *J* = 1.6 Hz, 2H, Ar-H), 8.75 (t, *J* = 1.6 Hz, 1H, Ar-H).

Diethyl (*E*)-5-(4-dodecyloxyphenyl)diazenyl isophthalate (3L)



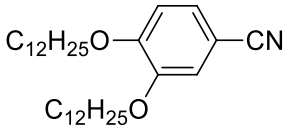
The azo intermediate **1** (0.99 g, 2.89 mmol), 1-bromododecane (**L-Br**) (0.94 g, 3.79 mmol), K_2CO_3 (0.80 g, 5.80 mmol) and butanone (40 mL) were added to a round-bottomed flask and stirred under reflux for 24 hours. After that, the system was cooled to room temperature and filtered under vacuum, and the K_2CO_3 was washed with butanone. Finally, the solvent was evaporated under reduced pressure and the product recrystallized from hexane, yielding 96%. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.88 (t, *J* = 6,7 Hz, 3H, CH_3), 1.17-1.52 (broad, 24H, -CH_2- and –$OCH_2C\underline{H}_3$), 1.83 (m, 2H, -CH_2-), 4.06 (t, *J* = 6.6 Hz, 2H, -CH_2O-), 4.46 (q, *J* = 7.1 Hz, 4H, –$OC\underline{H}_2CH_3$), 7.03 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.97 (d, *J* = 9.0 Hz, 2H, Ar-H), 8.69 (d, *J* = 1.6 Hz, 2H, Ar-H), 8.75 (t, *J* = 1.6 Hz, 1H, Ar-H).

(*E*)-5-(4-dodecyloxyphenyl)diazenyl isophthalic acid (4L)



In a 100 mL round-bottomed flask, a solution of **3L** (1.26 g, 2.47 mmol), KOH (0.50 g, 8.93 mmol), THF (55 mL) and ethanol (30 mL) was stirred under reflux for 24 hours. Afterwards, THF were removed under reduced pressure and the remaining ethanol solution was poured into 30 mL of distilled water. The solution was acidified to pH equal to 3 and heated. The product was recrystallized in the same mixture on cooling. Yield: 82 %. **^{1}H NMR** ($CDCl_3$ + drops of DMSO-d_6) δ ppm: 0.82 (t, *J* = 6.5 Hz, 3H, CH_3), 1.00-1.42 (broad, 18H, -CH_2-), 1.71 (m, 2H, -CH_2-), 4.04 (t, *J* = 6.4 Hz, 2H, -CH_2O-), 7.10 (d, *J* = 8.9 Hz, 2H, Ar-H), 7.94 (d, *J* = 8.9 Hz, Ar-H), 8.51 (d, *J* = 1.5 Hz, 2H, Ar-H), 8.57 (t, *J* = 1.5 Hz, 1H, Ar-H).

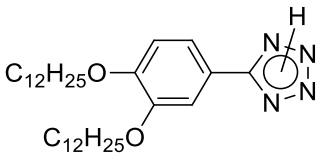
3,4-didodecyloxybenzonitrile (5)



To a round-bottomed flask, 3,4-dihydroxybenzonitrile (3.00 g, 22.20 mmol), 1-bromododecane (**L-Br**) (13.92 g, 55.90 mmol), K_2CO_3 (15.40 g, 111.59 mmol), TBAB (0.40 g, 1.24 mmol) and butanone (80 mL) were added and kept under reflux for 24 hours. Afterwards, the insoluble fraction was filtered and washed with hot butanone. Then the solvent was removed under reduced pressure and the remaining solid was dissolved in DCM and washed with water. The organic layer was dried with anhydrous Na_2SO_4 and the solvent removed. The remained material was recrystallized using acetonitrile yielding 95% of a white solid. **m.p.:** 81.9 ºC (ref. 79.8-82.8 ºC).[1] ; **^{1}H NMR** ($CDCl_3$) δ ppm: 0.88 (t, *J* = 6.8 Hz, 6H, CH_3), 1.20-1.55 (broad, 36H, -CH_2-), 1.83 (m, 4H, -CH_2-), 3.99 (t, *J* = 6.6 Hz, 2H, -CH_2O-), 4.03 (t, *J* = 6.6, 2H, -CH_2O-), 6.87 (d, *J* =

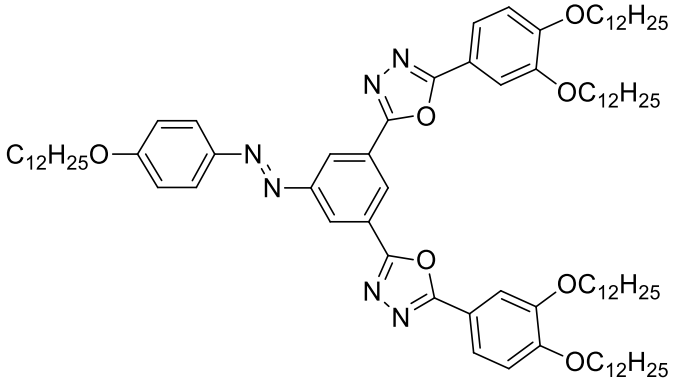
8.4 Hz, 1H, Ar-H), 7.07 (d, *J* = 1.9 Hz, 1H, Ar-H), 7.24 (dd, *J* = 1.9 and 8.4 Hz, 1H, Ar-H).

5-(3,4-didodecyloxyphenyl)tetrazole (6)



To a 250 mL round-bottomed flask with 3,4-didodecyloxybenzonitrile (**5**) (9.46 g, 20.08 mmol), NH_4Cl (3.24 g, 60.56 mmol), NaN_3 (3.93 g, 60.46 mmol) and 70 mL of DMF were added. Under magnetic stirring, the suspension was heated to 130 ºC for 24 hours and, afterward, cooled to room temperature and poured into 400 mL of water/ice. The mixture was acidified with HCl to pH = 3 and the precipitate filtered. The crude product was recrystallized from butanone yielding 9.60 g of a white solid (93 %). **m.p.**: 158.0 ºC (ref. 157.8-159.0 ºC).[1] **^{1}H NMR** ($CDCl_3$) δ ppm: 0.88 (t, *J* = 7.0 Hz, 6H, CH_3), 1.17-1.56 (broad, 36H, -CH_2-), 1.85 (m, 4H, -CH_2-), 4.05 (t, *J* = 6.5 Hz, 2H, -CH_2O-), 4.08 (t, *J* = 6.5 Hz, 2H, -CH_2O-), 6.97 (d, *J* = 8.3 Hz, 1H, Ar-H), 7.62 (dd, *J* = 1.9 and 8.3 Hz, 2H, Ar-H), 7.66 (d, *J* = 1.9 Hz, 2H, Ar-H).

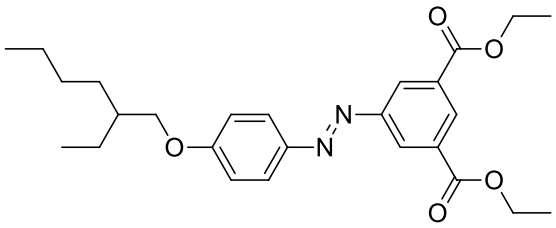
OXA-L



(*E*)-5-(4-dodecyloxyphenyl)diazenyl isophthalic acid (**4L**) (0.20 g, 0.44 mmol), 5-(3,4-didodecyloxyphenyl)tetrazole (**6**) (0.54 g, 1.05 mmol), DMAP (0.01 g, 0.08 mmol), anhydrous DCM (15 mL) and anhydrous DMF (2 mL) were added to a 50 mL round- bottom flask equipped with condenser and $CaCl_2$ drying tube. The solution was stirred and refluxed until the complete solubilization of the reagents. Then, DCC (0.23 g, 1.10 mmol) was added at once. The solution was kept under reflux for 24 hours. Subsequently, the solvent was removed under reduced pressure and the remaining solid was solubilized in 15 mL of ethanol and poured into a water/ice system. The crude product was purified by column chromatography using silica gel and a 5% solution of ethyl acetate in DCM as eluent. A further recrystallization in ethyl acetate resulted in 52% yield of an orange solid. **m.p.**: 96 ºC. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.88 (t, *J* = 6.6 Hz, 15H, CH_3), 1.21-1.59 (broad, 90H, -CH_2- and CH_3), 1.89 (m, 10H, -CH_2-), 4.11 (m, 10H, -CH_2O-), 7.03 (m, 4H, Ar-H), 7,70 (d, *J* = 1.8 Hz, 2H), 7.74 (d, *J* = 1.8 and 8.6 Hz, 2H

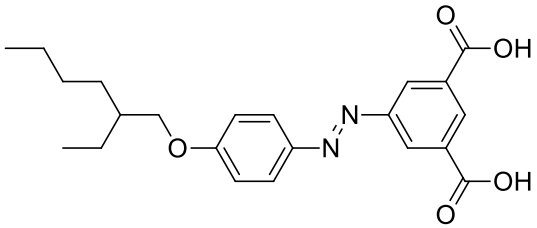
), 8.03 (d, *J* = 8.9 Hz, 2H, Ar-H), 8.76 (d, *J* = 1.5 Hz, 2H, Ar-H), 8.92 (t, *J* = 1.5 Hz, 1H, Ar-H).**^{13}C NMR** ($CDCl_3$) δ ppm: 14.13; 22.71; 26.03; 29.39; 29.65; 31.95; 69.19; 69.55; 111.78; 112.93; 114.94; 115.89; 120.80; 125.49; 126.13; 140.16; 140.99; 146.59; 149.44; 152.58; 153.63; 162.75; 163.08; 165.38. **HRMS**/APCI. m/z: $[M+H]^+$ predicted: 1392.0661; Measured: 1392.0707.

(*E*)-diethyl 5-{[4-(2-ethylhexyloxy)phenyl]diazenyl}isophthalate (7)



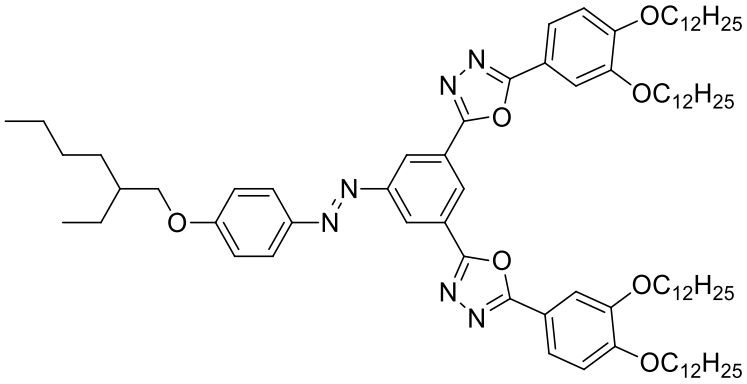
In a 100 mL round-bottom flask 1-bromo-2-ethylhexane (**R-Br**) (0.73 g, 3.78 mmol), diethyl (*E*)-5-(4-hydroxyphenyl)diazenyl isophthalate (**3**) (1.00 g, 2.92 mmol), K_2CO_3 (0.80 g, 5.80 mmol) and butanone (40 mL) were added and the solution refluxed for 24 hours. The remaining solid was removed by filtration and the solvent by evaporation under reduced pressure. The final product was isolated using column chromatography with silica gel and a 4:1 solution of DCM and hexane as eluent. The purified orange oily product yielded 88%. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.81-1.03 (m, 12H, CH_3), 1.45 (m, 1H, -CH-), 3.95 (d, *J* = 5.7 Hz, 2H, -CH_2O-), 4.46 (m, *J* = 7.2 Hz, 4H, -CH_2O-), 7.03 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.97 (d, *J* = 9.0 Hz, 2H, Ar-H), 8.69 (d, *J* = 1.6 Hz, 2H, Ar-H), 8.75 (t, *J* = 1.6 Hz, 1H, Ar-H).

(*E*)-5-[4-(2-ethylhexyloxy)phenyl]diazenyl isophthalic acid (4R)



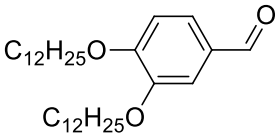
A solution of (*E*)-diethyl 5-{[4-(2-ethylhexyloxy)phenyl]diazenyl}isophthalate (**7**) (1.68, 3.70 mmol), KOH (1.00 g, 17.86 g), THF (40 mL) and ethanol (20 mL) was refluxed for 24 hours. After this period, the pH was lowered to approximately 3, and the resulting precipitate filtered. The crude product was recrystallized from acetonitrile yielding 90% of an orange solid. **^{1}H NMR** ($CDCl_3$ + drops of DMSO-d_6) δ ppm: 0.95 (m, 6H, CH_3), 1.20-1.62 (broad, 8H, -CH_2-), 1.77 (m, 1H, -CH-), 3.94 (d, *J* = 5.7 Hz, 2H, -CH_2O-), 7.03 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.94 (d, *J* = 9.0 Hz, 2H, Ar-H), 8.79 (d, *J* = 1.6 Hz, 2H, Ar-H), 8.79 (t, *J* = 1.6 Hz, 1H, Ar-H).

OXA-R



To a 50 mL round-bottomed flask, (*E*)-5-[4-(2-ethylhexyloxy)phenyl]diazenyl isophthalic acid (**4R**) (0.19 g, 0.49 mmol), $SOCl_2$ (0.50 mL, 6.89 mmol), anhydrous DCM (15 mL) and drops of anhydrous DMF were added and the mixture stirred and refluxed for 4 hours. Then, excess of solvent and $SOCl_2$ were removed under reduced pressure. To the flask containing the freshly prepared acyl chloride, 5-(3,4-didodecyloxyphenyl)tetrazole (**6**) (0.67 g, 1.30 mmol) and 10 mL of anhydrous pyridine were added and the solution refluxed for 24 hours. After that, the solution was cooled and poured into ice/water and the formed precipitate was separated by means of vacuum filtration. The crude product was purified by column chromatography using silica gel as a stationary phase and a gradient of DCM and ethyl acetate (100:0 – 95:5) as an eluent. A subsequent recrystallization from ethanol resulted in the target product with a 13% yield. **m.p.**: 100 ºC. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.80-1.05 (m, 22H, CH_3, -CH_2-), 1.21-1.50 (broad, 78H, -CH_2-), 1.89 (m, 7H, -CH-, -CH_2-), 3.97 (d, *J* = 5.6 Hz, 2H, -CH_2O-), 4.10 (t, *J* = 6.7 Hz, 4H, -CH_2O-), 4.14 (t, *J* = 6.7 Hz, 4H, -CH_2O-), 7.01 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.07 (d, *J* = 8.9 Hz, 2H, Ar-H), 7.70 (d, *J* = 1.8 Hz, 2H, Ar-H), 7.76, (dd, *J* = 1.8 and 8.4 Hz, 2H, Ar-H), 8.03 (d, *J* = 8.9 Hz, 2H, Ar-H), 8.77 (d, *J* = 1.6 Hz, 2H, Ar-H), 8.92 (t, *J* = 1.6 Hz, 1H, Ar-H). **HRMS**/APCI, m/z: $[M+H]^+$ predicted: 1336.0035; Measured: 1336.0105.

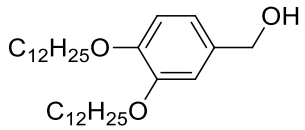
3,4-bis(dodecyloxy)benzaldehyde (**8**)



3,4-dihydroxybenzaldehyde (0.69 g, 5.07 mmol), K_2CO_3 (4.89 g, 35.43 mmol), TBAB (82.0 mg, 0.25 mmol), 1-bromododecane (**L-Br**) (3.15 g, 12.70 mmol) and butanone (50 mL) were added to a 100 mL round-bottom flask. The mixture was stirred under reflux for 24 hours and, after this period, the remaining insoluble solid (K_2CO_3) were removed by filtration. The solvent was evaporated under reduced pressure and the solid recrystallized over ethanol yielding 98% of the pure product. **m.p.**: 68 ºC (ref. 62-65 ºC).[2] **^{1}H NMR** ($CDCl_3$) δ ppm: 0.88 (t, *J* = 6.7 Hz, 6H, CH_3), 1,20.1,55 (broad, 36H, -CH_2-), 1.85 (m, 4H, -CH_2-), 4,05 (t, *J* = 6.5 Hz, 2H, -CH_2O-), 4.07 (t, *J* = 6.5 Hz,

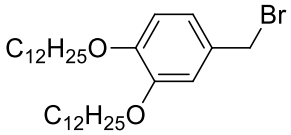
2H, -CH_2O-), 6.95 (d, *J* = 8.6 Hz, 1H, Ar-H), 7.38-7.44 (m, 2H, Ar-H), 9.83 (s, 1H, -COH).

[3,4-bis(dodecyloxy)phenyl]methanol (9)



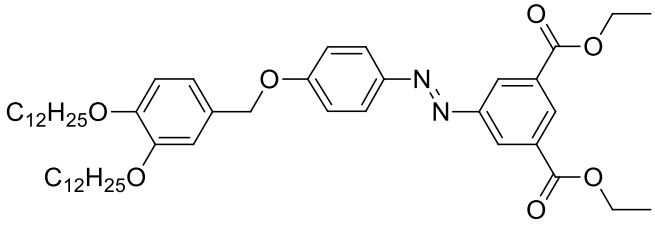
To a 150 mL round-bottom 3,4-bis(dodecyloxy)benzaldehyde (**8**) (1.0 g, 2.1 mmol), $NaBH_4$ (0.20 g, 5.26 mmol) and methanol (20 mL) were added and the resulting solution stirred under reflux overnight. Subsequently, it was acidified, cooled to room temperature and filtered. The obtained solid was recrystallized over methanol yielding 69 % of the pure product. **m.p.**: 44.1 ºC.[2] **^{1}H NMR (**$CDCl_3$ + drops of DMSO-d_6) δ ppm: 0.88 (t, *J* = 6.7 Hz, 6H, CH_3), 1.20-1.55 (broad, 36H, -CH_2-), 1.68-1.89 (m, 4H, -CH_2-), 3.98 (t, *J* = 6.6 Hz, 2H, -CH_2O-), 3.99 (t, *J* = 6.6 Hz, 2H, -CH_2O-), 4.59 (s, 2H, -CH_2O-), 6.83-6.95 (m, 3H, Ar-H).

4-(bromomethyl)-1,2-bis(dodecyloxy)benzene (Bn-Br)



In a 125 round-bottom flask, a solution of [3,4-bis(dodecyloxy)phenyl]methanol (**9**) (0.48 g, 1.01 mmol) and anhydrous DCM (60 mL) was kept in an ice bath and 1.0 mol L^{-1} of PBr_3 (3.30 mL) was slowly added. After one hour, the solution was heated to room temperature and kept stirring for another 3 hours. Then, the solution was poured in a 100 mL water/ice system, the product extracted with DCM, dried with anhydrous Na_2SO_4 and the solvent removed under reduced pressure. The resulting product was directly used in the next reaction.

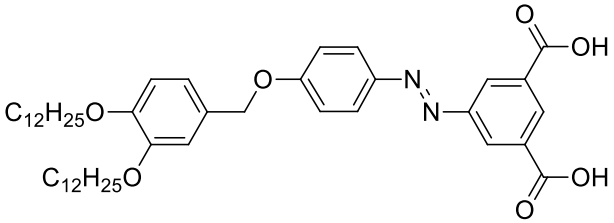
Diethyl (*E*)-5-[4-(3,4-didodecyloxybenzyloxy)phenyl]diazenylisophthalate (10)



A 125 mL round-bottom flask containing 4-(bromomethyl)-1,2-bis(dodecyloxy)benzene (**Bn-Br**) (1.00 mmol), diethyl (*E*)-5-(4-hydroxyphenyl)diazenyl isophthalate (**3**) (0.36 g, 1.05 mmol), K_2CO_3 (0.36 g, 2.63 mmol) and butanone (40 mL) was refluxed for 24 hours. After that it was poured into a water/ice system (70 mL) and the product extracted with ethyl acetate. The product was recrystallized for a mixture of ethanol and water. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.88 (t, *J* = 6.7 Hz, 6H, CH_3), 1.21-1.51

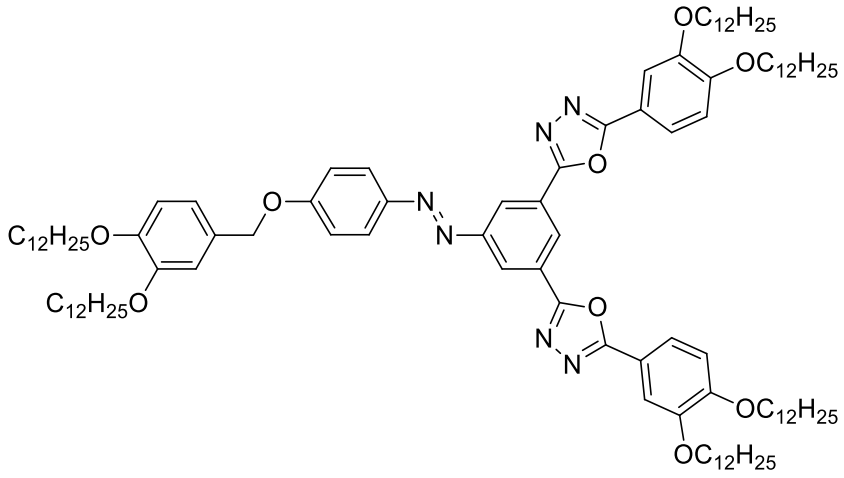
(broad, 38H, -CH_2-), 1.83 (m, 8H, -CH_2-), 4.01 (t, *J* = 6.5 Hz, 2H, -CH_2O-), 4.02 (t, *J* = 6.5 Hz, 2H, -CH_2O-), 4.44 (t, *J* = 7.1 Hz, 2H, -CH_2O-), 4.48 (t, *J* = 7.1 Hz, 2H, -CH_2O-), 5,07 (s, 2H, -CH_2O-), 6.89 (dd, *J* = 1.8 and 8.9 Hz, 1H, Ar-H), 6.93 (d, *J* = 8.9 Hz, 1H, Ar-H), 6.99 (d, *J* = 1.8 Hz, 1H, Ar-H) , 7.11 (d, *J* = 8.9 Hz, 2H, Ar-H), 7.98 (d, *J* = 8.9 Hz, 2H, Ar-H), 8.70 (d, *J* = 1.6 Hz, 2H, Ar-H), 8.75 (t, *J* = 1.6 Hz, 2H, Ar-H).

(*E*)-5-(4-(3,4-didodecyloxybenzyloxy)phenyl)diazenylisophthalic acid (4Bn)



The compound diethyl (*E*)-5-[4-(3,4-didodecyloxybenzyloxy)phenyl] diazenylisophthalate (**10**) (0.70 g, 0.93 mmol), THF (40 mL) and ethanol (20 mL) were added in a 140 mL round-bottom flask. Then 0.21 g (3.75 mmol) of KOH dissolved in 5 ml of water was added slowly. After three hours of reflux, the THF was removed under reduced pressure and the remained solution was poured into water (50 mL). The solution was added with ethyl acethate (30 mL) and extracted two more times. Afterwards the combined organic layers were evaporated under reduced pressure and the product was recrystallized from ethanol:water (2:1) yielding 86 % of an orange solid. **^{1}H NMR** ($CDCl_3$ com drops de DMSO-d_6) δ ppm: 0.88 (t, *J* = 6.7 Hz, 6H, CH_3), 1.16-1.61 (broad, 36H, -CH_2-), 1.83 (m, 4H, -CH_2-), 4.01 (m, 4H, -CH_2O-), 5.06 (s, 2H, -CH_2O-), 6.86-7.01 (m, 2H, Ar-H), 7.10 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.21 (s, 1H, Ar-H), 7.97 (d, *J* = 8.4 Hz, 2H, Ar-H), 8.74 (s, 2H, Ar-H), 8.83 (s, 1H, Ar-H).

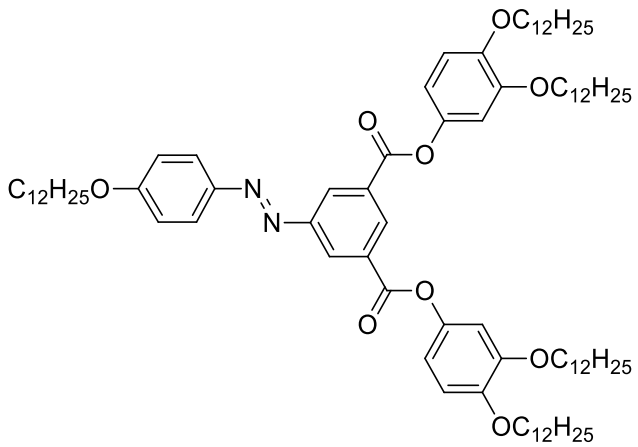
OXA-Bn



In a 50 mL round-bottom flask the (*E*)-5-[4-(3,4-didodecyloxybenzyloxy)phenyl]diazenylisophthalic acid (**4Bn**) (0.15 g, 0.09 mmol), 5-(3,4-didodecyloxyphenyl)tetrazole (**6**) (0.13 g, 0.26 mmol), DMAP (2.6 mg, 0.02 mmol), anhydrous DCE (15 mL) and anhydrous DMF (1.5 mL) were added and kept at 40 ºC.

After the complete solubilization of the material, DCC (0.06 g, 0.3 mmol) was added to the solution and heated until 98 ºC. The mixture was stirred for 24 hours and after that the solvent was removed under reduced pressure. The remained solid was dissolved into hot ethanol (15 mL) and poured into a water/ice system (20 mL). The precipitaded solid was filtrated and subjected to a chromatographic column using silica gel and DCM with 5 % ethyl acetate as eluent. The separated product was recrystallized from ethanol/water yielding 18% of an orange solid. **m.p.**: 80 ºC. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.88 (m, 18H, CH_3), 1.15-1.55 (broad, 108H, -CH_2-), 1.87 (m, 12H, -CH_2-), 4.02 (t, *J* = 6.6 Hz, 2H, -CH_2O-), 4.03 (t, *J* = 6.6 Hz, 2H, -CH_2O-), 4.10 (t, *J* = 6.5 Hz, 2H, -CH_2O-), 4.14 (t, *J* = 6.5 Hz, 2H, -CH_2O-), 5.09 (s, 2H, -CH_2O-), 6.91 (d, *J* = 9.2 Hz, 1H, Ar-H), 6.98 (dd, *J* = 1.6 and 9.2 Hz, 1H, Ar-H), 7.00 (d, *J* = 1.6 Hz, 1H, Ar-H), 7.02 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.15 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.70 (d, *J* = 2.1 Hz, 2H, Ar-H), 7.75 (dd, *J* = 2,1 and 8.3 Hz, 2H, Ar-H), 8.05 (d, *J* = 9.0 Hz, 2H, Ar-H), 8.78 (d, *J* = 1.7 Hz, 2H, Ar-H), 8.93 (t, *J* = 1.7 Hz, 1H, Ar-H). **^{13}C NMR** ($CDCl_3$ with drops of DMSO-d_6) δ ppm: 21.53, 31.24, 32.49, 36.01, 40.41, 41.24, 45.13, 44.48, 45.07, 45.94, 46.22, 46.87, 47.23, 47.95, 72.00, 79.49, 89.57, 101.39, 123.47, 123.59, 123.98, 127.51, 128.64, 131.57, 132.14, 139.54, 150.94, 151.43, 152.22, 153.78, 157.21, 160.55, 167.55, 171.37, 172.66. **HRMS**/APCI, m/z (%): $[M+H]^+$ predicted: 1682.2906; Measured: 1682.2930.

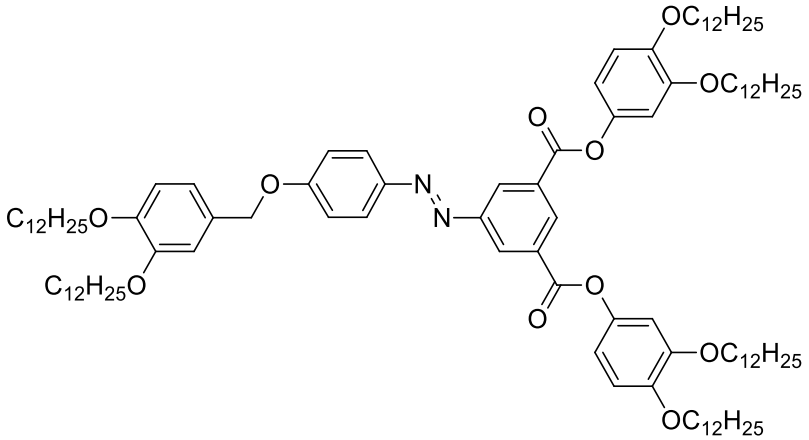
EST-L



A solution of (*E*)-5-(4-dodecyloxyphenyl)diazenyl isophthalic acid (**4L**) (0.24 g, 0.52 mmol), 3,4-didodecyloxyphenol (**11**) (0.24 g, 0.02 mmol), DMAP (2.5 mg, 0.02 mmol), anhydrous DCM (40 mL) and anhydrous DMF (0.5 mL) was stirred at room temperature, after that it was added with DCC (0.11 g, 0,55 mmol). The system was maintained at this condition for 48 hours. Afterwards the solvent was removed under reduced pressure and the product isolated using a chromatography column with silica gel and a solution of DCM and hexane (1:1), yielding 52 % of an orange solid after recrystallization from ethanol. **m.p.**: 55 ºC. **^{1}H NMR** ($CDCl_3$) δ ppm: 0,88 (m, 15H, -CH_3), 1.21-1.57 (broad, 90H, -CH_2-), 1.83 (m, 10H, -CH_2-), 4.01 (m, 10H, -CH_2O-), 6.79 (dd, *J* = 2.5 and 8.3 Hz, 2H, Ar-H), 6.81 (dd, *J* = 2,5 Hz, 2H, Ar-H) 6.92 (d, *J* = 8.3 Hz, 2H, Ar-H), 7.03 (d, *J* = 8.4 Hz, 2H, Ar-H), 8.00 (d, *J* = 8.4 Hz, 2H, Ar-H), 8.90 (s, 2H,

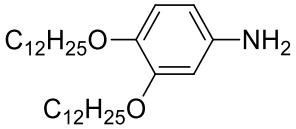
Ar-H), 9.03 (s, 1H, Ar-H). **HRMS**/APCI, m/z (%): $[M+H]^+$ predicted: 1344.0436; Measured: 1344.0478.

EST-Bn



To a 125 mL round-bottom flask was added (*E*)-5-[4-(3,4-didodecyloxybenzyloxy)phenyl]diazenylisophthalic acid (**4Bn**) (0.30 g, 0.40 mmol), DMAP (4 mg, 0.03 mmol) and anhydrous DCM (40 mL) and the solution was stirred at room temperature. The solution was subjected to magnetic stirring and 0.45 g (0.97 mmol) of 3,4-didodecyloxyphenol (**11**) previously dissolved in 10 ml of anhydrous DCM was added slowly. Then 0.21 g (1.01 mmol) of DCC dissolved in 10 ml of anhydrous DCM was subsequently added. The solution was stirred for 24 hours and afterwards the solvent was removed under reduced pressure. The target product was purified using column chromatography with silica gel and DCM as eluent, and then recrystallized from ethanol, yielding 50% of the product. **m.p.**: 79 ºC. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.88 (m, 18H, CH_3), 1.15-1.55 (broad, 108H, -CH_2-), 1.87 (m, 12H, -CH_2-), 4.02 (t, *J* = 6.6 Hz, 2H, -CH_2O-), 4.03 (t, *J* = 6.6 Hz, 2H, -CH_2O-), 4.10 (t, *J* = 6.5 Hz, 2H, -CH_2O-), 4.14 (t, *J* = 6.5 Hz, 2H, -CH_2O-), 5.09 (s, 2H, -CH_2O-), 6.88 (dd, 1H, Ar-H) 6.90 (d, 1H, Ar-H), 6.97 (d, *J* = Hz, 2H, Ar-H), 7.12 (d, *J* = 9.0 Hz, 2H, Ar-H), 8.00 (d, *J* = 9.0 Hz, 2H, Ar-H), 8.90 (d, *J* = 1.7 Hz, 2H, Ar-H), 9.03 (t, *J* = 1.7 Hz, 1H, Ar-H). **^{13}C NMR** ($CDCl_3$ with drops of DMSO-d_6) δ ppm: 17.94, 29.58, 31.88, 35.75, 38.32, 39.00, 44.13, 44.34, 44.49, 45.78, 46.02, 46.63, 46.87, 47.22, 71.61, 83.31, 88.88, 92.84, 120.00, 121.85, 122.67, 126.19, 127.93, 130.74, 133.68, 137.48, 146.58, 148.24, 153.37, 154.99, 156.51, 159.91, 166.77, 170.52, 171.62. **HRMS**/ APCI, m/z (%): $[M+H]^+$ predicted: 1634.2682; Measured: 1634.2723.

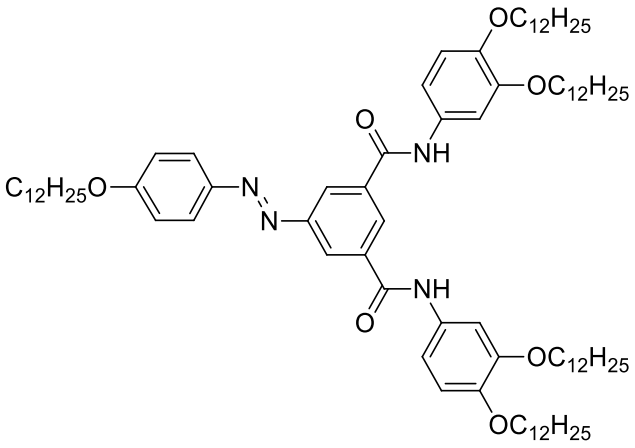
3,4-bis(dodecyloxy)aniline (12)



A mixture of 1,2-bis(dodecyloxy)-4-nitrobenzene (1.23 g, 2.51 mmol), THF (50 mL) and Pd/C (0.24 g, 5% [m/m]) were added an appropriate flask and submitted to

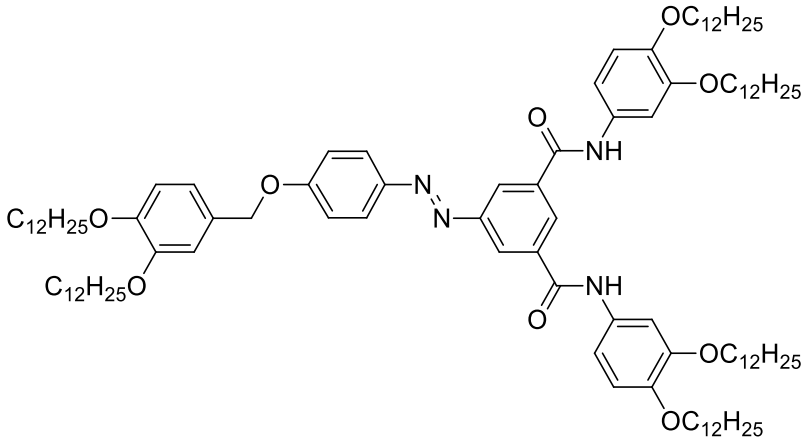
catalytic hydrogenation for 3 hours. After that the catalyst was removed by filtration in celite and the solvent was removed under reduced pressure, yielding 100 % of the product, which was employed in the next step without further purifications. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.88 (t, *J* = 6.8 Hz, 6H, CH_3), 1.20-1.55 (broad, 36H, -CH_2-), 1.79 (m, 4H, -CH_2-), 3.89 (t, *J* = 6.6 Hz, 2H, -CH_2O-), 3.93 (t, *J* = 6.6, 2H, -CH_2O-), 6.20 (dd, *J* = 1.9 and 8.4 Hz, 1H, Ar-H), 6.30 (d, *J* = 1.9 Hz, 1H, Ar-H), 6.73 (d, *J* = 8 4 Hz, 1H, Ar-H).

AMD-L



To a 50 mL round-bottom flask were added diethyl (E)-5-(4-dodecyloxyphenyl)diazenyl isophthalate (**3L**) (0.30 g, 6.79 mmol), 3,4-bis(dodecyloxy)aniline (**12**) (0.69 g, 50 mmol) DMAP (16.0 mg, 0.13 mmol), anhydrous DCE (25 mL) and anhydrous DMF (3 mL). After the complete solubilization, DCC (0.35 g, 1.70 mmol) was added to the system and stirred under reflux overnight. Afterwards, the solvent was removed under reduced pressure and the orange solid was purified by column chromatography using silica gel and DCM as eluent. Later, recrystallization from methyl isobutyl ketone and isopropanol, yielded 7% of the product. **m.p.**: 102 °C. **^{1}H NMR** ($CDCl_3$) δ ppm: 0.88 (m, 15H, -CH_3), 1.21-1.57 (broad, 90H, -CH_2-), 1.83 (m, 10H, -CH_2-), 4.01 (m, 10H, -CH_2O-), 6.86 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.00 (d, *J* = 9.0 Hz, Ar-H), 7.09 (dd, *J* = 2.1 and 9.0 Hz, 2H, Ar-H), 7.42 (d, *J* = 2.1 Hz, 2H, Ar-H), 7.91 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.25 (s, 2H, Ar-H), 8.37 (s, 1H, Ar-H), 8.43 (s, 2H, -CONH-). **^{13}C NMR** ($CDCl_3$) δ ppm: 14.12; 22.70; 26.06; 29.37; 29.64; 31.93; 69.36; 69.87; 107.61; 112.91; 113.64; 113.79; 114.24; 115.28; 120.55; 125.38; 128.63; 131.47; 144.45; 147.17; 149.88; 153.15; 162.21; 164.23. **HRMS**/ APCI, m/z (%): $[M+H]^+$ predicted: 1342.0756; Measured: 1342.0790.

AMD-Bn



To a 50 mL round-bottom flask equipped with a condenser, (*E*)-5-[4-(3,4-didodecyloxybenzyloxy)phenyl]diazenylisophthalic acid (**4Bn**) (0.16 g, 0.20 mmol), DMAP (13.4 mg, 0.03 mmol), 3,4-bis(dodecyloxy)aniline (**12**) (0.23 g, 0.52 mmol), anhydrous DCM (15 mL) and anhydrous DMF (2 mL) were added. After the solubilization at room temperature, DCC (0.12 g, 0.50 mmol) was added. The system was stirred at room temperature for 24 hours and then the solvent was evaporated under reduced pressure. The solid obtained was purified by column chromatography using silica gel and DCM as the eluent. Finally, the product was dissolved in DCM and poured into ethanol to force its precipitation, and filtered. After that the solvent was evaporated under reduced pressure, yielding 28% of an orange solid. **m.p.**: 87 ºC .**^{1}H NMR** ($CDCl_3$ com drops de DMSO-d_6) δ ppm: 0.88 (m, 18H, CH_3), 1.15-1.58 (broad, 108H, -CH_2-), 1.83 (m, 12H, -CH_2-), 4.01 (m, 12H, -CH_2O-), 5.08 (s, 2H, -CH_2O-), 6.73-6.93 (broad, 7H, Ar-H), 6.96 (d, *J* = 8.3 Hz, 2H, Ar-H), 6.88 (d, *J* = 8.7 Hz, 2H, Ar-H), 6.90 (d, *J* = 8.6 Hz, 1H, Ar-H), 6.99 (dd, *J* = 1.8 and 6.3 Hz, 2H, Ar-H), 7.12 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.27 (dd, *J* = 2.2 and 8.6 Hz, 2H, Ar-H) 7.58 (d, *J* = 2.2 Hz, 2H, Ar-H), 7.97 (d, *J* = 9.0 Hz, 2H, Ar-H), 8.63 (s, 2H, Ar-H), 8.68 (s, 1H, Ar-H), 9.90 (s, 2H, -CONH-). **^{13}C NMR** ($CDCl_3$ with drops of DMSO-d_6) δ ppm: 18.87, 27.36, 30.73, 34.02, 34.33, 36.58, 44.02, 44.16, 44.38, 45.53, 45.67, 45.77, 46.04, 46.69, 73.66, 74.02, 74.55, 112.46, 117.75, 118.48, 118.56, 119.28, 120.02, 125.38, 129.34, 129.82, 133.48, 137.37, 141.26, 150.50, 151.44, 153.94, 154.02, 157.55, 166.62, 169.37. **HRMS**/APCI, m/z (%): $[M+H]^+$ predicted: 1632.3001; Measured: 1634.2723.

5. REFERENCES

1. Westphal, E., Bechtold, I. H. & Gallardo, H. Synthesis and Optical/Thermal Behavior of New Azo Photoisomerizable Discotic Liquid Crystals. *Macromolecules* **43**, 1319–1328 (2010).

2. Hope-Ross, K. A., Heiney, P. A. & Kadla, J. F. A new family of bent-core C2-symmetric liquid crystals. *Canadian Journal of Chemistry* **88**, 639–645 (2010).