Supplementary Data

**Self-assembled star-shaped liquid crystals based on 1,3,5-trihydroxybenzene with pendant alkyloxylated azobenzene arms**

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1. Experimental

Reagents and chemicals

The starting materials such as phloroglucinol (anhydrous), 4-aminobenzoic acid, 1-bromohexane, 1-bromoheptane, 1-bromooctane, 1-bromononane and 1-bromodecane were obtained from (Aldrich) and were used without further purification. All final compounds were purified by column chromatography with Silica gel 60 (Merck). All organic solvents (acetone, dichloromethane, ethyl acetate, hexanes) used in chemical synthesis and for purification the reaction products were purchased from Chemical Company (Romania) were dried, distilled (conventional methods) or used as bought.

Characterization

FT-IR measurement

Fourier transform infrared (FT-IR) spectra for all the intermediate and target compounds were recorded using a Nicolet Magna 550 spectrometer (NaCl crystal window) in the frequency range 4000 – 400 cm-1 with samples embedded in KBr discs.

NMR measurement

NMR spectra were recorded in CDCl3 at 298 K on a BrukerÒ Avance DRX 400 MHz spectrometer. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS) as internal standard.

MS Measurement

Mass spectra were acquired with a RapiFlex MALDI Time of Flight (TOF/TOF) tissue typer (Bruker Daltonics) equipped with a Smartbeam 3D laser and controlled by the FlexControl 4.0 software package. The mass spectrometer was operated using positive polarity in reflectron mode and spectra were acquired in the range of m/z 100–1600.

Phase transition temperatures and enthalpy values

The phase transitions temperatures along with its associated enthalpy change were registered on a Mettler Toledo DSC1. Heating and cooling cycles were run at rates of 10 0C/min or 5 0C/min under nitrogen atmosphere, with sample measured in closed lid aluminum pans.

Liquid crystalline texture observation

The optical microscopy studies were carried out with a Carls Zeiss Axioskop 40 polarizing microscope equipped with a Linkam heating stage connected with a Linksys 32 temperature control unit in conjunction with Qimaging/Retiga-1000R camera for image capture. The textures of the compounds were observed using polarized light with a cross polarizer whereby the studied sample was prepared in a thin film sandwiched between a glass slide and coverslip.

Thermal analysis

All the thermal analysis were run in the same conditions, on 2.8 - 4.3 mg samples on a Mettler-Toledo® TGA SDTA851® derivatograph in N2 atmosphere, with a flow rate of 20 ml/min and a heating rate of 10 0C/min from 25 to 900 °C.

Synthesis

Synthesis was carried out following a convergent strategy outlined in Scheme 1. The arms (4-(4-alkoxyphenylazo)-benzoic acid chlorides Aa-e) were prepared using diazotization/coupling reactions, followed by Williamson etherification. In the final step, the obtained acyl chlorides Aa-e were attached to the resorcinol, providing the target molecules 1a-e. High purity of all materials was achieved by recrystallization or column chromatography after each single step, which was proven by 1H-NMR, 13C-NMR and MS.

**General synthesis of compounds 1a-1e**

In a round bottom flask, a mixture containing phloroglucinol (1.08 mmol) and triethylamine (TEA), (0.780 ml, 5.59 mmol) were dissolved in 30 ml tetrahydrofurane (THF). To the reaction mixture cooled to 0 °C, 4-((4-alkyloxy)phenyl)diazenyl)benzoyl chlorides (Aa÷e) (4.28 mmol) were added, followed by refluxing for 12 hours. Upon cooling to room temperature, triethyl ammonium salt was filtered out and washed three times with THF. After removing the solvent by distillation, the obtained residue was purified by CC/silicagel, dichloromethane : hexanes= 20 : 1.

Benzene-1,3,5-triyl tris(4-((4-(hexyloxy)phenyl)diazenyl)benzoate) (**1a**)

Quantities: phloroglucinol (1.087 mmol, 0.137 g), 4-((4-hexyloxy)phenyl)diazenyl) benzoyl chloride (4.280 mmol, 1.473 g). Yield: 64 % (0.739 g), orange crystals. 1H NMR (400 MHz, CDCl3, δ / ppm): 8.32 (d, 6H, ArH), 7.98-7.95 (m, 12H, ArH), 7.25 (s, 3H, ArH), 7.02 (d, 6H, ArH), 4.05 (t, 6H, -O-CH2-), 1.83 (qv, 6H, -CH2-), 1.49 (qv, 6H, -CH2-), 1.36 (m, 12H, -CH2-), 0.92 (t, 9H, -CH3). 13C-NMR (101 MHz, CDCl3, δ / ppm): 163.96 (esteric), 162.53, 155.95, 151.59, 146.87, 131.29, 129.86, 125.35, 122.60, 114.84 (aromatic), 68.46 (-O-CH2-), 31.55, 29.12, 25.67, 22.58, 14.01 (aliphatic). FT-IR (KBr, cm-1): 1739.79 (ν O-C=O). Calculated: m/z 1051.25 (M+H)+. Found: m/z 1051.560 [(M+H)+, 100%].

Benzene-1,3,5-triyl tris(4-((4-(heptyloxy)phenyl)diazenyl)benzoate) (**1b**)

Quantities: phloroglucinol (1.087 mmol, 0.137 g), 4-((4-heptyloxy)phenyl)diazenyl) benzoyl chloride (4.288 mmol, 1.536 g). Yield: 63 % (0.750 g), orange crystals. 1H-NMR (400 MHz, CDCl3, δ / ppm): 8.32 (d, 6H, ArH), 7.98-7.95 (m, 12H, ArH), 7.24 (s, 3H, ArH), 7.02 (d, 6H, ArH), 4.05 (t, 6H, -O-CH2-), 1.82 (qv, 6H, -CH2-), 1.48 (qv, 6H, -CH2-), 1.32 (m, 18H, -CH2-), 0,90 (t, 9H, -CH3). 13C-NMR (101 MHz, CDCl3, δ / ppm): 163.97 (esteric), 162.53, 155.96, 151.59, 146.87, 131.30, 129.85, 125.34, 122.60, 114.84 (aromatic), 68.46 (-O-CH2-), 31.75, 29.15, 29.03, 25.96, 22.58, 14.06 (aliphatic). FT-IR (KBr, cm-1): 1739.79 (ν O-C=O). 1739.79 (ν O-C=O). Calculated: m/z 1093.34 (M+H)+. Found: m/z 1093.606 [(M+H)+, 100%]

Benzene-1,3,5-triyl tris(4-((4-(octyloxy)phenyl)diazenyl)benzoate) (**1c**)

Quantities: phloroglucinol (1.087 mmol, 0.137 g), 4-((4-octyloxy)phenyl)diazenyl) benzoyl chloride (4.280 mmol, 1.593 g). Yield: 55 % (0.680 g), orange crystals. 1H-NMR (400 MHz, CDCl3, δ / ppm): 8.33 (d, 6H, ArH), 7.98-7.95 (m, 12H, ArH), 7.25 (s, 3H, ArH), 7.02 (d, 6H, ArH), 4.05 (t, 6H, -O-CH2-), 1.83 (qv, 6H, -CH2-), 1.48 (qv, 6H, -CH2-), 1.30 (m, 24H, -CH2-), 0.90 (t, 9H, -CH3). 13C-NMR (101 MHz, CDCl3, δ / ppm): 163.97 (esteric), 162.55, 155.96, 151.60, 146.87, 131.30, 129.87, 125.36, 122.60, 114.85 (aromatic), 68.48 (-O-CH2-), 31.80, 29.33, 29.21, 29.16, 26.00, 22.64, 14.08 (aliphatic). FT-IR (KBr, cm-1): 1739.79 (ν O-C=O). Calculated: m/z 1135.42 (M+H)+. Found: m/z 1135.65179 (ν O-C=O). Calculated: m/z 1135.42 (M+H)+. Found: m/z 1135.651 [(M+H)+, 100%].

Benzene-1,3,5-triyl tris(4-((4-(nonyloxy)phenyl)diazenyl)benzoate) (**1d**)

Quantities: phloroglucinol (1.087 mmol, 0.137 g), 4-((4-nonyloxy)phenyl)diazenyl) benzoyl chloride (4.280 mmol, 1.653 g). Yield: 75 % (0.967 g), orange crystals. 1H-NMR (400 MHz, CDCl3, δ / ppm): 8.33 (d, 6H, ArH), 7.98-7.95 (m, 12H, ArH), 7.25 (s, 3H, ArH), 7.02 (d, 6H, ArH), 4.05 (t, 6H, -O-CH2-), 1.83 (qv, 6H, -CH2-), 1.48 (qv, 6H, -CH2-), 1.30 (m, 30H, -CH2-), 0.89 (t, 9H, -CH3). 13C-NMR (101 MHz, CDCl3, δ / ppm): 163.96 (esteric), 162.54, 155.95, 151.59, 146.87, 131.29, 129.86, 125.35, 122.59, 114.84 (aromatic), 68.47 (-O-CH2-), 31.86, 29.50, 29.37, 29.23, 29.15, 25.99, 22.65, 14.08 (aliphatic). FT-IR (KBr, cm-1): 1739,79 (ν O-C=O).

Benzene-1,3,5-triyl tris(4-((4-(decyloxy)phenyl)diazenyl)benzoate) (**1e**)

Quantities: phloroglucinol (1.087 mmol, 0.137 g), 4-((4-decyloxy)phenyl)diazenyl) benzoyl chloride (4.280 mmol, 1.713 g). Yield: 73 % (0.968 g), orange crystals. 1H-NMR (400 MHz, CDCl3, δ / ppm): 8.33 (d, 6H, ArH), 7.99-7.95 (m, 12H, ArH), 7.25 (s 3H, ArH), 7.02 (d, 6H, ArH), 4.05 (t, 6H, -O-CH2-), 1.82 (qv, 6H, -CH2-), 1.48 (qv, 6H, -CH2-), 1.28 (m, 36H, -CH2-), 0.88 (t, 9H, -CH3). 13C-NMR (101 MHz, CDCl3, δ / ppm): 163.97 (esteric), 162.51, 155.95, 151.57, 146.85, 131.30, 129.83, 125.34, 122.59, 114.82 (aromatic), 68.45 (-O-CH2-), 31.88, 29.55, 29.37, 29.30, 29.15, 25.99, 22.67, 14.11 (aliphatic). FT-IR (KBr, cm-1): 1741.72 (ν O-C=O). Calculated: m/z 1219.58 (M+H)+. Found: 1219.760 [(M+H)+, 100%].

1. Thermogravimetric investigation

