

Supplementary Materials

Novel Sulphonic Acid Liquid Crystal Derivatives; Experimental, Computational and Optoelectric Characterizations

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1. Materials

4-Hexyloxybenzoic acid, 4-octyloxybenzoic acid, 4-decyloxybenzoic acid, 4-dodecyloxybenzoic acid 4-hydroxybenzaldehyde, and 4-aminobenzenesulfonic acid, were purchased from Sigma Aldrich (Germany) while the dichloromethane, *N,N'*-dicyclohexylcarbodiimide (DCC), ethanol and 4-dimethylaminopyridine (DMAP) were purchased from Aldrich (Wisconsin, USA).

2.2.2. Synthesis of (*E*)-4-((4-((4-(alkoxy)benzoyl)oxy)benzylidene)amino)benzenesulfonic acid, *Sn*

A mixture of imine compound **3** (2.77g, 10 mmol) and the appropriate 4-alkoxy benzoic acid derivatives **4** (10 mmol for each) in dry methylene chloride (25 mL) containing *N, N'*-dicyclohexylcarbodiimide (DCC, 10 mmol) and few crystals of

4-dimethylaminopyridine (DMAP), as catalyst, were left to stand for 72 hours at room temperature with continuous stirring. The solid separated was then filtered off and the solution evaporated. The solid residue obtained was recrystallized from ethanol to give TLC pure products. The purity of the prepared samples was checked with thin-layer chromatography (TLC) using TLC sheets coated with silica gel (E Merck), and CH₂Cl₂/CH₃OH (9:1) as eluent, whereby only one spot was detected by a UV-lamp. Infrared spectra (IR), ¹H-NMR, and elemental analyses for compounds investigated were consistent with the structures assigned. ¹H-NMR data showed the expected integrated aliphatic to aromatic proton ratios in all compounds investigated.

The physical data of products **Sn** are listed below:

(E)-4-((4-((4-(Hexyloxy)benzoyl)oxy)benzylidene)amino)benzenesulfonic acid (S6).

Yield: 92.3%; mp 216.0 °C, FTIR (ν, cm⁻¹): 3423 (OH), 3034, 2944, 2928, 2917 (C-H), 1733 (C=O), 1626 (C=N), 1574 (C=C), 1346 (S=O stretching). ¹H-NMR (400 MHz, DMSO): δ/ppm: 0.84 (s, 1H, SO₃H), 0.96-1.02 (t, 3H, CH₃(CH₂)₃CH₂CH₂O-), 1.06-1.57 (m, 6H, CH₃(CH₂)₃CH₂CH₂O-), 1.66-1.78 (m, 2H, CH₃(CH₂)₃CH₂CH₂O-), 4.00-4.02 (t, 2H, CH₃(CH₂)₃CH₂CH₂O-), 6.71-6.73 (d, 2H, Ar-H), 6.98-7.00 (d, 2H, Ar-H), 7.49-7.51 (d, 2H, Ar-H), 7.64-7.66 (d, 2H, Ar-H), 7.89-7.91 (d, 2H, Ar-H), 8.09-8.12 (d, 2H, Ar-H), 10.08 (s, 1H, CH=N) ppm; ¹³C-NMR (400 MHz, DMSO): δ/ppm: 13.94, 22.09 (CH₃), 25.16, 25.32, 28.56, 32.29 (CH₂), 67.74 (CH₂-O), 106.83, 114.01, 119.18, 125.94, 126.8, 128.50, 129.63, 135.32, 143.14, 144.52 (Ar-C), 155.37, 156.62 (C=N), 161.13 (Ar-C-OR), 164.81 (C=O) ppm. Anal. Calcd. for C₂₆H₂₇NO₆S (481.56): C, 64.85; H, 5.65; N, 2.91. Found: C, 64.70; H, 5.52; N, 2.81%.

(E)-4-((4-((4-(Octyloxy)benzoyl)oxy)benzylidene)amino)benzenesulfonic acid (S8).

Yield: 89.1%; mp 205.0 °C, FTIR (ν, cm⁻¹): 3414 (OH), 3031, 2946, 2922, 2918 (C-H), 1730 (C=O), 1612 (C=N), 1551 (C=C), 1352 (S=O stretching). ¹H-NMR (400 MHz, DMSO): δ/ppm: 0.82 (s, 1H, SO₃H), 0.97-1.03 (t, 3H, CH₃(CH₂)₅CH₂CH₂O-), 1.02-1.55 (m, 10H, CH₃(CH₂)₅CH₂CH₂O-), 1.69-1.73 (m, 2H, CH₃(CH₂)₅CH₂CH₂O-), 3.99-4.01 (t, 2H, CH₃(CH₂)₅CH₂CH₂O-), 6.70-6.72 (d, 2H, Ar-H), 6.96-6.99 (d, 2H, Ar-H), 7.35-7.38 (d, 2H, Ar-H), 7.60-7.62 (d, 2H, Ar-H), 7.77-7.79 (d, 2H, Ar-H), 8.02-8.05 (d,

2H, Ar-H), 9.85 (s, 1H, CH=N) ppm. Anal. Calcd. for C₂₈H₃₁NO₆S (509.61): C, 65.99; H, 6.13; N, 2.75. Found: C, 65.74; H, 6.02; N, 2.59%.

(E)-4-((4-((4-(Decyloxy)benzoyl)oxy)benzylidene)amino)benzenesulfonic acid (S10).

Yield: 88.2%; mp 213.0 °C, FTIR (ν , cm⁻¹): 3418 (OH), 3027, 2944, 2928, 2917 (C-H), 1731 (C=O), 1626 (C=N), 1575 (C=C), 1346 (S=O stretching). ¹H-NMR (400 MHz, DMSO): δ /ppm: 0.81 (s, 1H, SO₃H), 0.96-1.02 (t, 3H, CH₃(CH₂)₇CH₂CH₂O-), 1.06-1.57 (m, 14H, CH₃(CH₂)₇CH₂CH₂O-), 1.66-1.78 (m, 2H, CH₃(CH₂)₇CH₂CH₂O-), 4.01-4.03 (t, 2H, CH₃(CH₂)₇CH₂CH₂O-), 6.57-6.59 (d, 2H, Ar-H), 6.87-6.89 (d, 2H, Ar-H), 6.98-7.00 (d, 2H, Ar-H), 7.49-7.51 (d, 2H, Ar-H), 7.89-7.91 (d, 2H, Ar-H), 8.06-8.07 (d, 2H, Ar-H), 9.74 (s, 1H, CH=N) ppm; ¹³C-NMR (400 MHz, DMSO): δ /ppm: 15.53 (CH₃), 22.85, 24.95, 25.84, 27.17, 29.01, 30.92, 32.14, 33.83 (CH₂), 66.91 (CH₂-O), 107.25, 116.38, 125.12, 127.31, 129.51, 131.82, 132.64, 136.89, 145.07, 148.68 (Ar-C), 156.00, 158.31 (C=N), 159.74 (Ar-C-OR), 164.86 (C=O) ppm. Anal. Calcd. for C₃₀H₃₅NO₆S (537.67): C, 67.02; H, 6.56; N, 2.61. Found: C, 67.17; H, 6.50; N, 2.43%.

(E)-4-((4-((4-(Dodecyloxy)benzoyl)oxy)benzylidene)amino)benzenesulfonic acid (S12).

Yield: 90.6%; mp 221.0 °C, FTIR (ν , cm⁻¹): 3424 (OH), 3029, 2941, 2928, 2916 (C-H), 1724 (C=O), 1626 (C=N), 1554 (C=C), 1347 (S=O stretching). ¹H-NMR (400 MHz, DMSO): δ /ppm: 0.80 (s, 1H, SO₃H), 0.97-1.02 (t, 3H, CH₃(CH₂)₉CH₂CH₂O-), 1.06-1.55 (m, 18H, CH₃(CH₂)₉CH₂CH₂O-), 1.61-1.76 (m, 2H, CH₃(CH₂)₉CH₂CH₂O-), 3.92-3.98 (t, 2H, CH₃(CH₂)₉CH₂CH₂O-), 6.50-6.52 (d, 2H, Ar-H), 6.80-6.82 (d, 2H, Ar-H), 6.96-6.98 (d, 2H, Ar-H), 7.42-7.45 (d, 2H, Ar-H), 7.80-7.82 (d, 2H, Ar-H), 8.00-8.03 (d, 2H, Ar-H), 9.69 (s, 1H, CH=N) ppm. Anal. Calcd. for C₃₂H₃₉NO₆S (565.72): C, 67.94; H, 6.95; N, 2.48. Found: C, 67.79; H, 6.74; N, 2.25%.

2.2. Characterization

Perkin-Elmer B25 (Perkin-Elmer, Inc., Shelton, CT USA) spectrophotometer was used for infrared spectra measurements. Varian EM 350L 500 MHz spectrometer (Oxford, UK) was used for recording ¹H-NMR spectra using tetramethyl silane as internal standard in CDCl₃; the chemical shift values recorded as δ (in ppm units).

Thermo Scientific Flash 2000 CHS/O Elemental Analyzer, Milan, Italy was used for Elemental analyses.

TA Instruments Co. (Q20 Differential Scanning Calorimeter, DSC; USA) was used for recording phase transitions. DSC calibration was carried out using lead and indium to calibrate the melting temperatures and enthalpies. Samples of 2–3 mg were used in aluminum pans for DSC investigation. The heating rate was 10°C/min in nitrogen gas as an inert atmosphere (30 ml/min). All transitions temperatures were measured from the second heating scan.

Transition temperatures for the prepared compounds were checked and phases identified by Polarized optical microscope (POM, Wild, Germany) attached with Mettler FP82HT hot stage.

The optical absorbance and transmission spectra of the investigated array, **Sn**, were measured using a Perkin Elmer spectrophotometer (Lambda 950 UV-VIS-NIR) over a wavelength range of 250 to 1500 nm. A Keithley measurement source device (Model 4200 SMU) was used to test the electrical properties of the examined films. The current-voltage (I–V) characteristics of the Sn series were recorded by varying the applied voltage (V) from -10 V to 10 V with different scan steps, 1V to 0.005V.

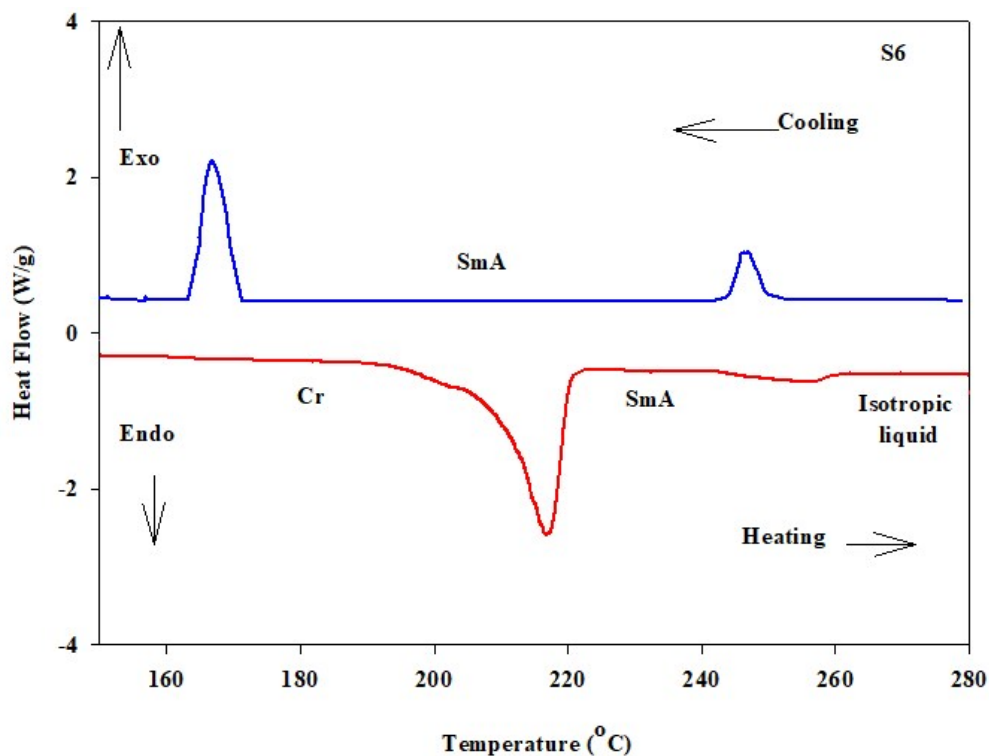


Figure S1. DSC thermograms of compounds **S6** at a rate of $\pm 10^\circ\text{C}/\text{min}$ recorded from heating and cooling scans.

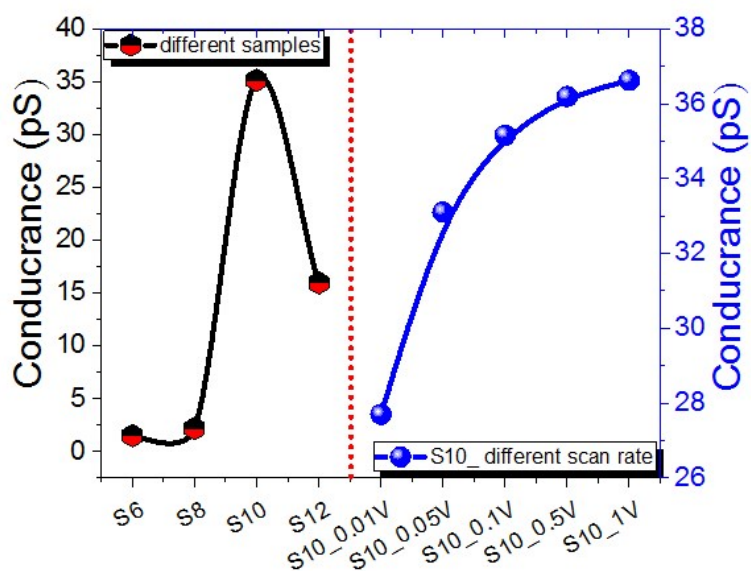


Figure S2. (A) electric conductance for the **Sn** series and **S10** sample at different step scans.

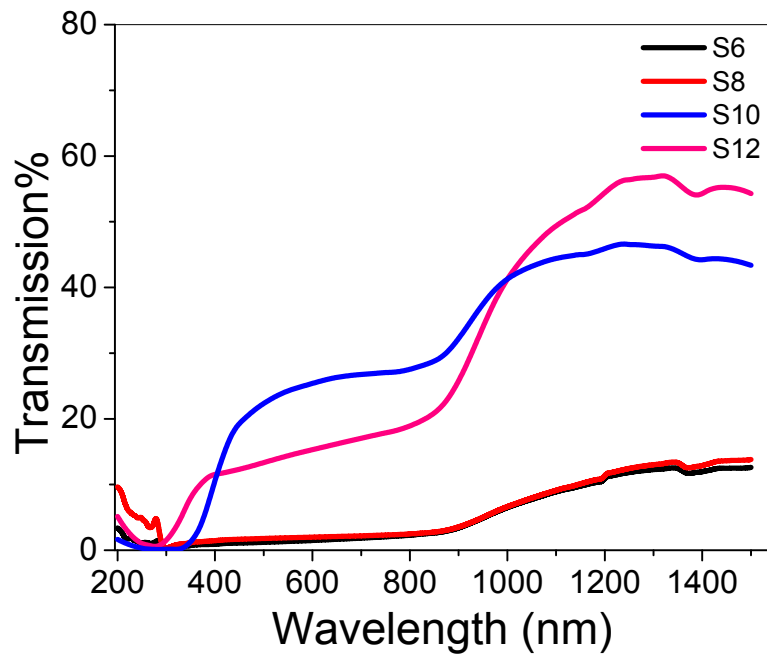


Figure S3. Optical transmittance of Sn films.

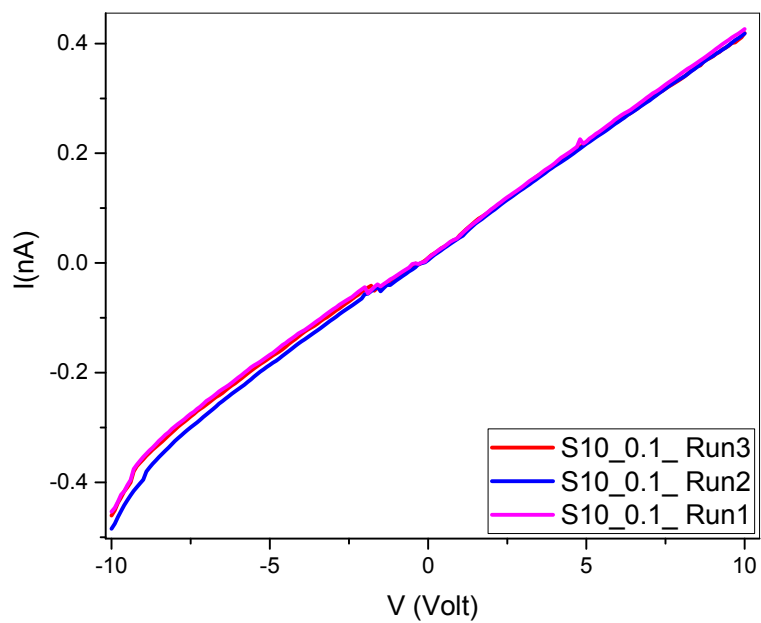


Figure S4. Current-Voltage characteristics of S10 for different runs.