Supplementary Data

Induced Phases of New H-bonded Supramolecular Liquid Crystal Complexes; Mesomorphic and Geometrical Estimation

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1. Experimental

1.1. Materials

4-Hexyloxyaniline, 4-octyloxyaniline, 4-hexadecyloxyaniline were purchased from Sigma Aldrich (Germany). The 4-formylbenzoic acid and ethanol were purchased from Aldrich (Wisconsin, USA).

1.2. Synthesis

Compounds **An** were prepared according to the following scheme:
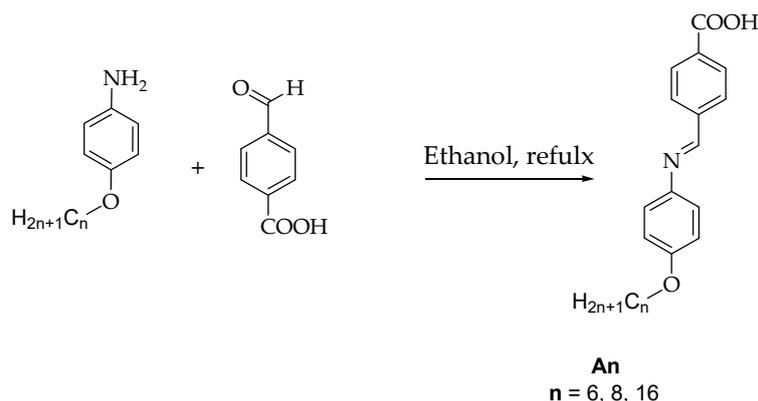
Scheme 1. Synthesis of 4-[4(alkoxy)phenylimino)methyl]benzoic acid (**An**).

1.2.1. Synthesis of 4-[4(alkoxy)phenylimino)methyl]benzoic acid (**An**)

An equimolar amount of 4-formylbenzoic acid (610 mg, 4.1 mmol) and 4-hexyloxyaniline (790 mg, 4.1 mmol) in ethanol (10 mL) were refluxed for two hours. The reaction mixture was allowed to cool and the separated product was filtered. The obtained solid was recrystallized from ethanol [1–3].

Yield: 93.0%; mp 190.0 °C, FTIR ($\acute{v}$, cm^{-1}): 2930–2864 (CH$_2$ stretching), 1678 (C=O), 1616 (C=N),1597 (C=C), 1490 (C–O$_{Asym}$), 1235 (C–O $_{Sym}$). ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.03 (s, 1H, CH=N), 8.13 (d, *J* = 8.5 Hz, 2H, ArH), 7.97 (d, *J* = 8.5 Hz, 2H, ArH), 7.40 (d, *J* = 8.4 Hz, 2H, ArH), 6.99 (d, *J* = 8.6 Hz, 2H, ArH), 4.05 (t, *J* = 6.5 Hz, 2H, CH$_3$(CH$_2$)$_3$CH$_2$CH$_2$), 1.91 – 1.76 (m, 2H,CH$_3$(CH$_2$)$_3$CH$_2$CH$_2$), 1.58–1.56 (m, 6H, CH$_3$(CH$_2$)$_3$CH$_2$CH$_2$), 0.88 (t, *J* = 6.6 Hz, 3H, CH$_3$(CH$_2$)$_3$CH$_2$CH$_2$). ^{13}C NMR (101 MHz, CDCl$_3$) δ 191.62, 169.63, 159.57, 139.62, 134.29, 130.78, 129.60, 124.37, 115.44, 115.42, 68.39, 31.55, 29.22, 25.64, 22.60, 14.05. Elemental analyses: Found (Calc.): C, 73.79 (73.82); H, 7.11 (7.12); N, 4.29 (4.30).

1.2.2. Instruments

TA Instruments Co. Q20 Differential Scanning Calorimeter (DSC; USA) were using for calorimetric measurements. The DSC was calibrated using the melting temperature and enthalpy of indium and lead. DSC investigation was carried out for small samples (2–3 mg) placed in aluminum pans. All measurements were achieved at a heating rate of 10 °C/min in inert atmosphere of nitrogen gas (30 mL/min) and all transition recorded from the second heating scan.

Transition temperatures for the individual components and their 2:1 associated complexes were determined by DSC, and the types of the mesophase identified by a standard polarized optical microscope (POM, Wild, Germany) attached with Mettler FP82HT hot stage. The temperature is measured by a thermocouple attached to the temperature controller. Measurements were made twice and the results have accuracy in transition temperature within ± 0.2 °C.

1.2.3. Characterizations

Molecular structures of **Im** were checked with thin-layer chromatography using TLC and elemental analyses. The structure was confirmed by FTIR (Nicolet iS 10 Thermo scientific), and ^{1}H-NMR spectroscopy (Varian EM 350L 300 MHz spectrometer, Oxford, UK).

1.2.4. Computational Method and Calculations

The theoretical calculations for the investigated compounds were carried out by Gaussian 09 software [4]. DFT methods using the B3LYP 6-311G basis set was selected for the calculations. The geometries were optimized by minimizing the energies with respect to all geometrical parameters without imposing any molecular symmetry constraints. The structures of the optimized geometries had been drawn with Gauss View [5]. Moreover, the calculated frequencies were carried out using the same level of theory. The frequency calculations showed that all structures were stationary points in the geometry optimization method with none imaginary frequency.
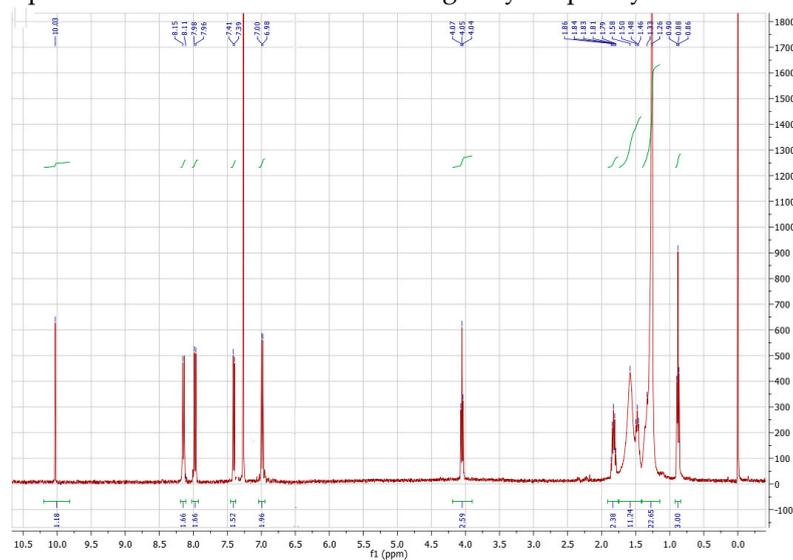
Figure S1. ^{1}H NMR of 4-[4-(hexyloxy)phenylimino)methyl]benzoic acid (A6).
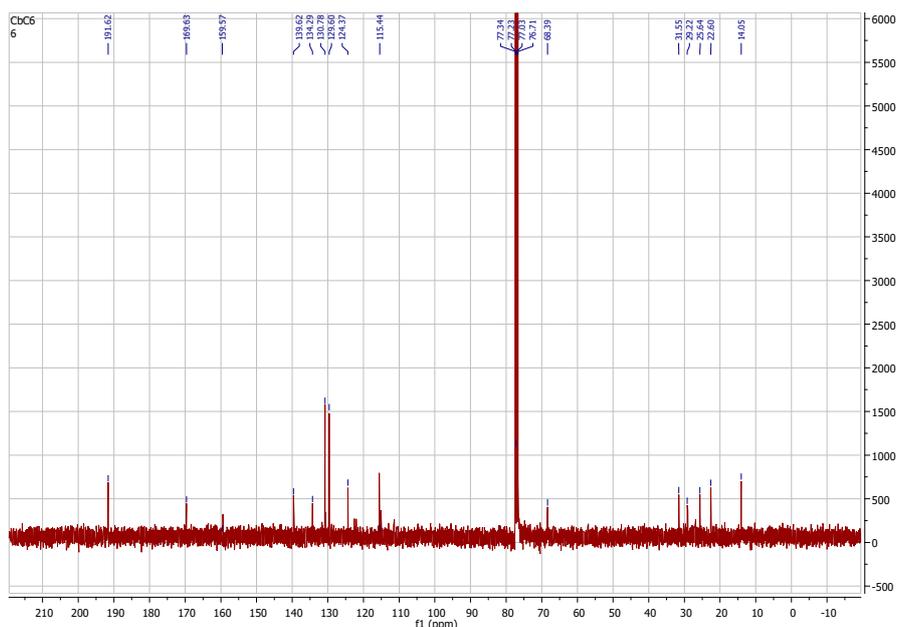
Figure S2. C[13] NMR of 4-[4-(hexyloxy)phenylimino)methyl]benzoic acid (A6).

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