

Induced Smectic Phases from Supramolecular H-Bonded Complexes based on Non-Mesomorphic Components

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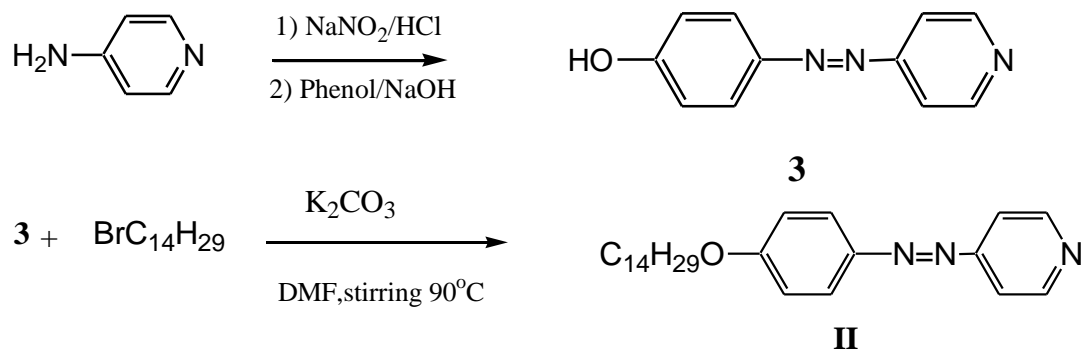
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1. Materials

Palmitic, oleic and linolic acids were obtained from Sigma Aldrich (Germany).

1.1. Preparation of 4-tetradecyloxyphenylazo pyridine (II)



1.2. Preparation of 4-(pyridin-4-yl)diazenylphenol (3)

To a solution of 4.0 g (0.058 mol) of sodium nitrite in 20 ml water, 5.0 g (0.053 mol) phenol in 45 ml of 10% sodium hydroxide solution (0.1125 mol) was added with stirring while cooling both solutions to 0°C. The resulting solution was added to a cooled solution of 4-aminopyridine (6.0 g, 0.064 mol) in 25 ml (0.25 mol) concentrated hydrochloric acid and 16 ml water with stirring for 10 minutes below 0°C. Subsequently, a saturated solution of sodium carbonate was added to adjust the pH of the mixture to about 6. A yellow dye is formed. Azopyridine component (II) was synthesized through the synthetic pathway shown [40]:

1.3. Alkylation of 4-(Pyridin-4-yl)diazenylphenol

4-(Pyridin-4-yl-diazenyl)phenol (1.00 g, 5.01 mmol, 1.0 eq.) and K₂CO₃ (1.04 g, 7.53 mmol, 1.5 eq.) were dissolved in 50 mL DMF. Then alkyl bromide (5.01 mmol, 1.0 eq.) was added and the mixture was stirred at 90 °C for 2 h. The reaction mixture was poured into 150 mL water and the suspension was extracted with ethyl acetate (30 mL * 2 times). The organic layers were combined and washed with 5% NaHCO₃(aq) and brine. After drying over MgSO₄, the solvent was removed under reduced pressure. The obtained residue was purified by column chromatography.

4-tetradecyloxyphenylazo pyridine, **II**

Yield: 83 % M.P: 66 °C ¹H NMR (300 MHz, CDCl₃) δ= 8.76 (d, J = 5.2 Hz, 2H), 7.96 (d, J = 9.0 Hz, 2H), 7.72 (d, J = 5.8 Hz, 2H), 7.06 – 7.00 (d, J = 9.0 Hz, 2H), 4.06 (t, J = 6.5 Hz, 2H), 1.89 – 1.77 (m, 2H), 1.47 (m, 2H), 1.31 (m, 8H), 0.89 (t, J = 6.8 Hz, 2H).
¹³C NMR (75 MHz, CDCl₃) δ 163.19, 157.82, 150.94, 146.86, 125.81, 116.43, 115.05, 68.68, 31.95, 29.45, 29.36, 29.27, 26.14, 22.79, 14.23.

2. Characterizations and Instrumentation

Purity of all prepared compounds were checked with thin-layer chromatography using TLC-sheets coated with silica gel (E. Merck), whereby single spots were detected by a UV-lamp.

Molecular formulae of the prepared base compounds (**II**) were confirmed via elemental analyses, infrared, Mass spectra and ¹H-NMR spectroscopy. The results agreed with the proposed structures and with those reported in the literature [40].

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 1:1 complexes (**Ix/II**), were determined by DSC, and the types of the mesophase identified by a standard polarized light microscope (POM, Wild, Germany) attached with Mettler FP82HT hot stage. The temperature is measured by thermocouple attached to the temperature controller. Measurements were made twice and the results have accuracy in transition temperature within ± 0.2 °C.

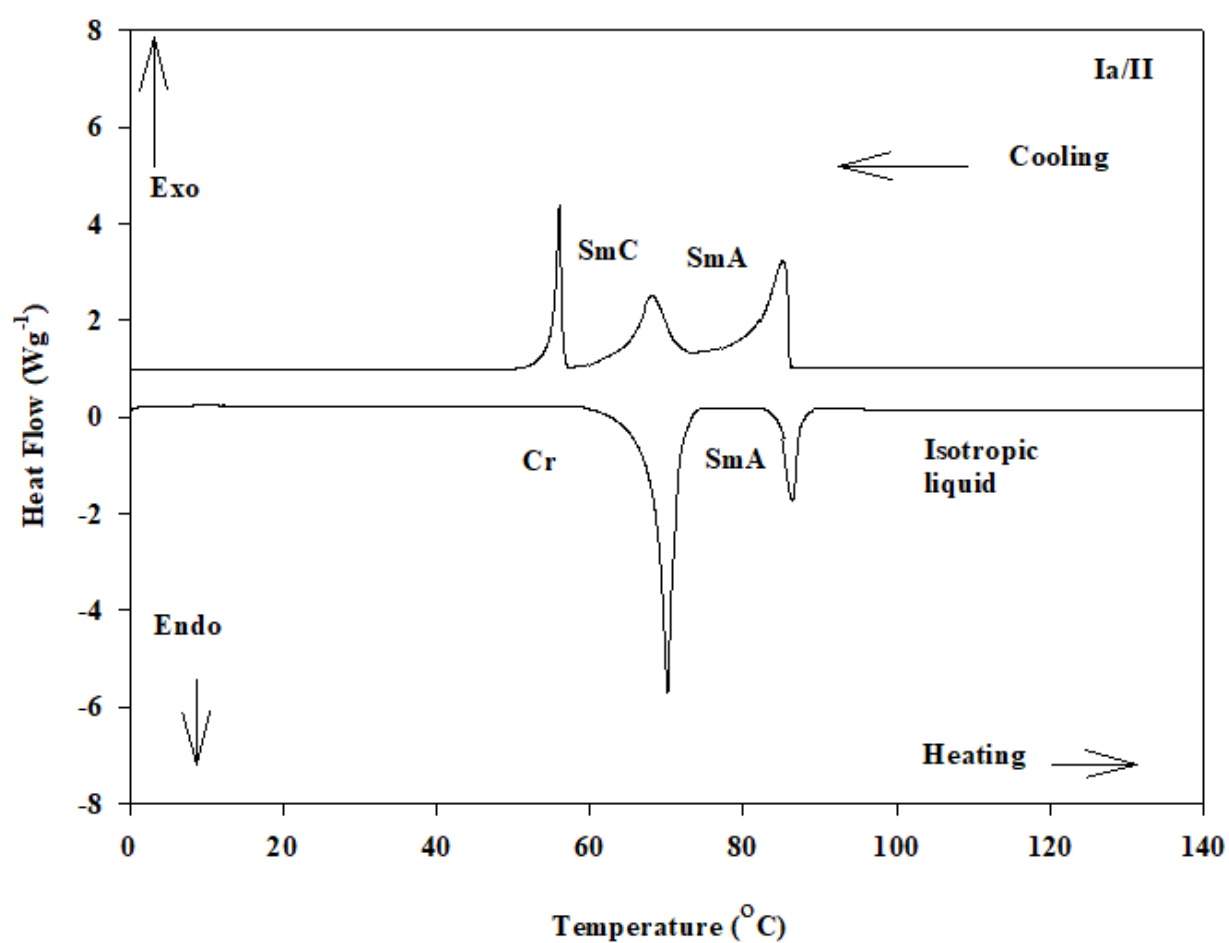


Figure S1. DSC thermograms of second heating/cooling rounds of Ia/II complex at heating rate $10\text{ }^{\circ}\text{C min}^{-1}$.

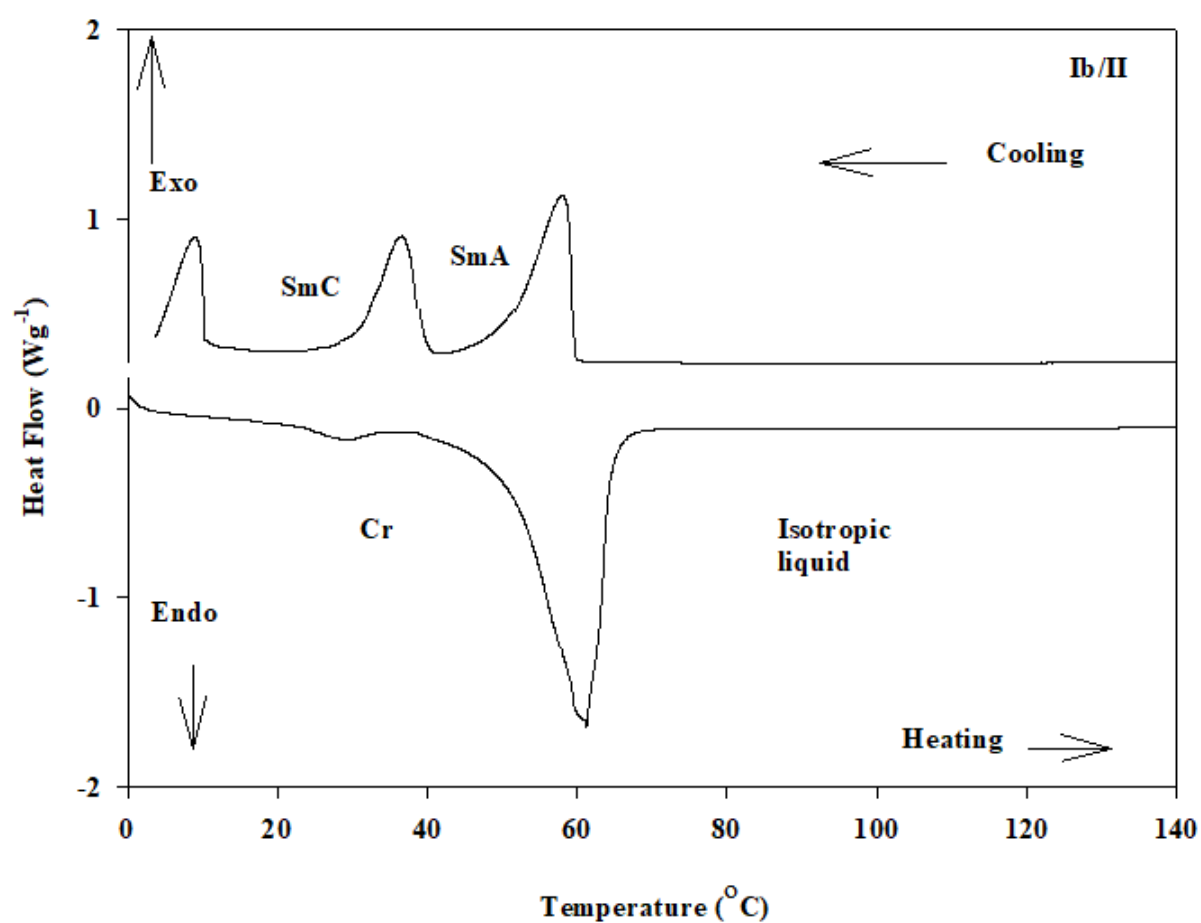


Figure S2. DSC thermograms of second heating/cooling rounds of Ib/II complex at heating rate $10^{\circ}\text{C min}^{-1}$.