

Molecular ordering in the high-temperature nematic phase of an all-aromatic liquid crystal

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Supplementary Information

Experimental

Materials. 4-Biphenylboronic acid and 2,6-dibromonaphthalene was purchased from Alfa Aesar. Tetrakis(triphenylphosphine)palladium(0) 99% and tetrahydrofuran (anhydrous >99.9%, inhibitor free) was obtained from Sigma Aldrich. All materials were used as received.

Analysis. FT-IR measurements were performed on PPNPP using a Perkin-Elmer 100 spectrometer in attenuated total reflection (ATR) mode. The background contribution was measured and subtracted automatically from the spectra by the software. The sample was scanned in the wavelength range between 4500 cm^{-1} and 500 cm^{-1} . An average of 15 scans were recorded. A Shimadzu GCMS QP2010S mass spectrometer equipped with an EI ion source filament at 200 °C and a direct inject mode and was used to record the mass spectrograph of PPNPP. The sample was directly introduced into the mass spectrometer and heated at 10 °C/min from 25 °C to 300 °C. The detector was used to scan in the range m/z 30 to 900. M^+ represents the molecular ion. Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer Sapphire DSC, which was calibrated with indium (99.99%) (m.p., 156.5 °C, $\Delta H=28.315$ J/g) and tin (99.99%) (m.p., 232.0 °C, $\Delta H=54.824$ J/g). A heat and cool cycle was performed using samples (~0.7 mg) in crimped Aluminum pans at a rate of 20 °C/min under a nitrogen atmosphere between 25 °C to 540 °C. In principle all-aromatic compounds are very stable, but in our case we could not confirm that by thermogravimetric analysis (TGA) because of the high volatility of our non-polar compound. However repeated DSC experiments in sealed sample pans showed that the phase transitions were stable, even after being held for a few hours at 425 °C.

Synthesis of 2,6-biphenyl naphthalene (PPNPP). A 25 mL 1-neck round bottom flask equipped with magnetic stir bar, reflux condenser and nitrogen inlet was charged with 2,6-dibromonaphthalene (0.31 g, 1.1 mmol), 5 mol% $\text{Pd}(\text{PPh}_3)_4$ (0.15 g, 0.13 mmol) and 10 mL THF. The yellow/orange solution was stirred for 5 min at room temperature. 4-Biphenylboronic acid (0.5 g, 2.5 mmol) was added together with 10 mL of a 2M Na_2CO_3 solution. The reaction mixture was refluxed for 16 h. After cooling the reaction mixture to room temperature, 20 mL water was added and the solids were collected by filtration, washed with excess water and acetone. The crude product was dried and dissolved in hot 1,2,4-trichlorobenzene and filtered over a short Si-gel/celite patch to remove Pd(0). Upon cooling, colourless, plate-like crystals of PPNPP formed. The crystals were collected and recrystallized two more times from hot 1,2,4-trichlorobenzene. Yield: 0.44 g (92%). IR ν_{max} : 3054, 1486, 1409, 893, 842, 828, 766 cm^{-1} ; MS m/z : 432 (M^+) (95%), 433 (35), 216 (43), 77

(13); DSC Heating: K–K' (367 °C, $\Delta H = 18.1$ J/g), K'–SmA (387 °C, $\Delta H = 61.5$ J/g), SmA–N (417 °C, ΔH not measurable), N–I (489 °C, $\Delta H = 4.72$ J/g); DSC Cooling: K–K' (354 °C, $\Delta H = -6.86$ J/g), K'–SmA (375 °C, $\Delta H = -13.2$ J/g), SmA–N (402 °C, ΔH not measurable), N–I (476 °C, $\Delta H = -1.22$ J/g).

Figure S1. FTIR Data

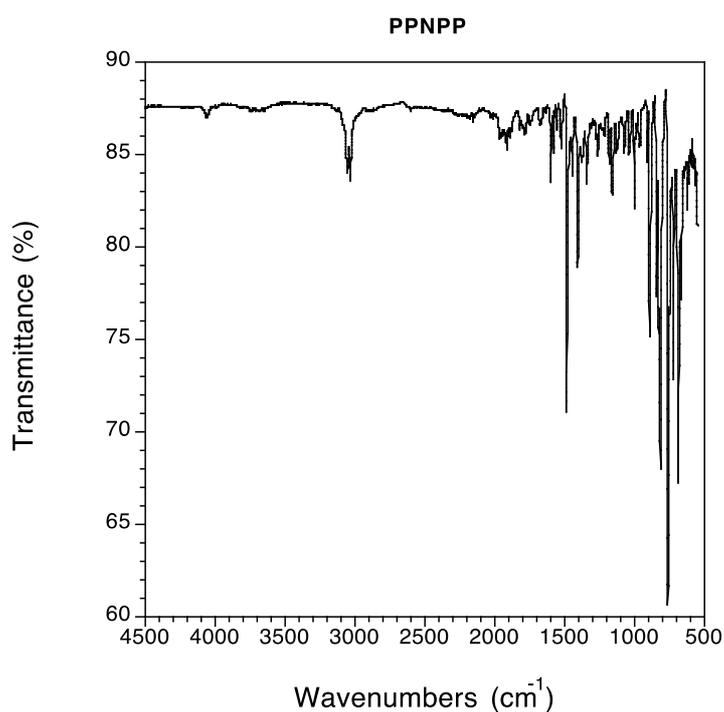


Figure S2. MS Data

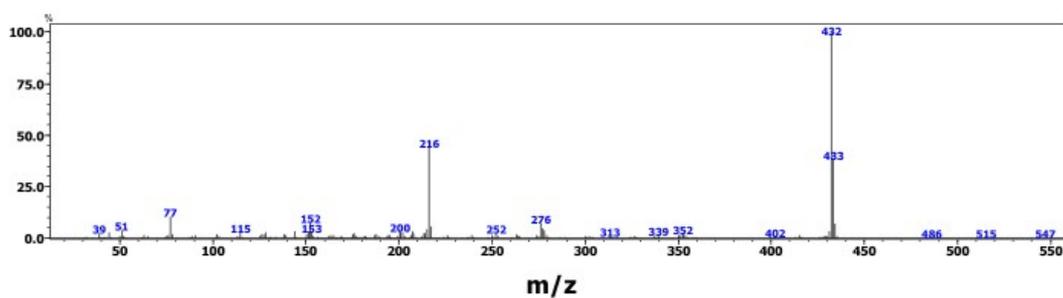


Figure S3. DSC Data

