Supporting Information

Synthesis of 1,7-Bis(2',3'-difluoro-4''-pentyl-[1,1':4',1''-terphenyl]-4-yl)heptane

Maria -Gabriella Tambac, Muhammad Salili, Cuiyu Zhang, Antal Jákli, Georg H. Mehl, Ralf Stannarius and Alexey Eremin

Preparation of heptanediyl dichloride (1): Heptanedioic acid (14.4 g, 0.09 mol) was dissolved in dry dichloromethane (200 ml) under nitrogen. Oxalyl chloride (30 ml, 44.3 g, 0.35 mol) was added followed by dry N, N'-dimethylformamide (1 drop) and gentle stirring. The nitrogen supply was turned off and the reaction was monitored by the evolution of gas. The reaction was stirred overnight and then refluxed for 2 hours until gas evolution had ceased. The solution was evaporated by vacuum distillation to yield crude nonanedioyl dichloride which was used immediately in the Friedel-Crafts acylation described below. Due to the instability of acyl chlorides the crude product was used immediately; no NMR spectra were recorded.

Preparation of 1,7-bis(4-bromophenyl)heptane-1,5-dione (2): Bromobenzene (50 ml, 37.4 g, 0.24 mol) was added to powdered aluminium chloride (12.5 g, 0.094 mol) and rapidly stirred under nitrogen for 1 hour. The crude heptanediyl dichloride was dissolved in bromobenzene (15ml, 22.4 g, 0.143 mol) and was added dropwise over a period of one hour. The temperature of the reaction was maintained below 45 °C during the addition. The reaction mixture was maintained at 40 °C and stirred overnight. The reaction was allowed to cool to ambient temperature and poured into a solution of concentrated hydrochloric acid (150ml) in ice water (600 ml). A small portion of dichloromethane was added to dissolve the suspended solids. The aqueous layer was extracted with dichloromethane several times and the organic extracts were dried over magnesium sulphate with rapid stirring overnight. The dichloromethane was evaporated under reduced pressure. The crude solid was recrystallised

Figure 1S. Synthetic scheme of 1,7-Bis(2',3'-difluoro-4''-pentyl-[1,1':4',1''-terphenyl]-4-yl)heptane.
from ethanol four times to yield 1,5-bis-(4-bromophenyl)heptane-1,7-dione. The yield was found to be 9.2 g, 42 %.

$^1$H NMR (400 MHz, CDCl$_3$, J/Hz): $\delta$ 7.81 (4H, d, $J = 8.6$); 7.59 (4H, d, $J = 8.6$); 2.92 (4H, t, $J = 7.3$); 1.69-1.76 (4H, m); 1.42-1.35 (2H, m).

Preparation of 1,7-bis-(4-bromophenyl)nonane (3): 1,5-Bis-(4-bromophenyl)heptane-1,5-dione (4.4 g, 0.01 mol) was dissolved in trifluoroacetic acid (30.75 ml, 45.79 g, 0.40 mol). Triethylsilane (8.3 ml, 6.05 g, 0.05 mol) was added dropwise over a period of one hour with rapid stirring and cooling in a water bath. The reaction mixture became turbid white after 1 hour. The reaction was stirred at ambient temperature for 48 hours. The reaction mixture was poured into a mixture of ice and water. Hexane was added and the aqueous layer was extracted in hexane four times. The organic extracts were combined and were dried over magnesium sulphate overnight. The solvent was then evaporated. The crude product was separated by column (silica) chromatography and yielded 1,5-bis-(4-bromophenyl)heptane. The yield was found to be 1.56 g, 38.1 %

$^1$H NMR (400 MHz, CDCl$_3$, J/Hz); $\delta$ 7.38 (4H, d, $J = 8.4$); 7.04 (4H, d, $J = 8.6$); 2.55 (4H, t, $J = 7.7$); 1.53-1.61 (4H, m); 1.24-1.35 (6H, m).

Preparation of 1,7-bis(2',3'-difluoro-4''-pentyl-[1,1':4',1''-terphenyl]-4-yl)heptane (4): A solution of 1,5-bis-(4-bromophenyl)heptane (0.5 g, 0.012 mol) and (2,3-difluoro-4'-pentyl-[1,1'-biphenyl]-4-yl)boronic acid (1.0 g, 0.03 mol) in a mixture of 1,2-dimethoxyethane (12 ml) and saturated aqueous solution of sodium hydrogen carbonate (18 ml) was thoroughly degassed with argon for 1 hour. Tetrakis(triphenylphosphine)palladium(0) 50 mg was added. The reaction was refluxed at 125 °C for 12 hours under stirring. The reaction was allowed to cool to room temperature. Water was added to the reaction. The aqueous solution was extracted with dichloromethane four times and dried over magnesium sulphate overnight. The solvent was evaporated and the crude product was separated by column chromatography and yielded 1,5-bis(2',3'-difluoro-4''-pentyl-[1,1':4',1''-terphenyl]-4-yl)nonane. The mobile phase was a hexane/dichloromethane gradient starting with pure hexane finishing at 50 % dichloromethane. The yield was found to be 0.60 g, 68 %.

$^1$H NMR (400 MHz, CDCl$_3$, J/Hz); $\delta$: 7.50 (8H, d, $J = 8.0$); 7.28 (4H, d, $J = 8.0$); 7.22 (4H, m); 2.64 (8H, t, $J = 8.0$); 1.62-1.70 (8H, m); 1.39-1.38 (14H, m); 0.91 (6H, t, $J = 7.1$).

$^{13}$C NMR (100 MHz, CDCl$_3$); $\delta$:C: 148.5, 143.1, 143.0, 132.0, 131.9, 129.5, 128.71, 128.68, 124.6, 35.7, 31.6, 31.3, 31.1, 29.3, 29.2, 22.6, 14.0.
Polarising microscopy textures

Figure 2S: POM studies between crossed polarizers on cooling (untreated glasses): a) N phase at 145 °C, schlieren texture. ; b) N_{tb} phase at 110 °C, rope texture ; Sm phase at 80 °C, modulated rope texture . d) Sm phase at 85 °C, focal conic domains.

Calorimetry data (DSC)
Rescaled with focus on the LC range.

Figure 3S: DSC traces (scans run at 10°Cmin⁻¹). Top: scaled to see full scan range, bottom rescaled to show LC range.
Accurate Mass

a)

b)

c)
Experimental Techniques

Optical studies were made using AxioImager D.1 polarising microscope (Carl Zeiss GmbH). Spatially resolved birefringence was measured using CRI Abrio (CRI, USA). X-ray diffraction were performed using Cu Kα radiation (0.1541 nm, data were collected using a Mar 345 image plate, the samples, kept at controlled temperatures in capillaries were magnetically aligned (~0.5 T) in a homebuilt. FF-TEM studies were carried out on a FEI Tecnai F20 microscope. KA(0.2) was sandwiched between two copper planchetters, heated up to the isotropic phase, and then cooled to the N_{ib} phase. After the equilibrium temperature was reached, the sample was quenched in liquid nitrogen. The frozen sample was transferred to the vacuum chamber of a freeze-fracture machine (BalTec BAF060), where a built-in microtome was used to knock off the top planchetter and create a fracture surface, which then was covered by 3–4 nm thick platinum layer deposited at 45°, and by a~20nm carbon film deposited at 90°. After the specimen was removed and warmed up, the liquid crystal was
dissolved by chloroform, thus creating a replica, which was collected on carbon-coated grid for TEM imaging.