

Dynamic Calorimetry and XRD Studies of the Nematic and Twist-Bend Nematic Phase Transitions in a Series of Dimers with Increasing Spacer Length

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S1 – Synthetic Information for DTC5C5

Synthesis of Synthesis of 1,5-Bis(2',3'-difluoro-4''-pentyl-[1,1':4',1''-terphenyl]-4-yl)pentane

The material was synthesized according to the procedure reported in:

M. G. Tamba, S. M. Salili, C. Zhang, A. Jáklí, G. H. Mehl, R. Stannarius, A. Eremin, "A fibre forming smectic twist-bend liquid crystalline phase", *RSC Adv.*, (2015), **5**, 11207. 10.1039/c4ra14669g

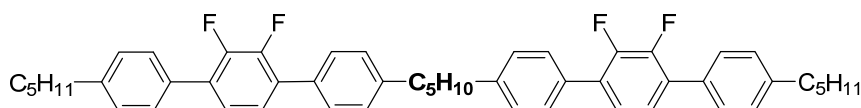


Figure S1 – Chemical structure of DTC5C5.

δ_{H} (400MHz; CD_2Cl_2) 7.52-7.46 (m, 8H), 7.31-7.26 (m, 8H), 7.26-7.22 (m, 4H), 2.70-2.61 (m, 8H), 1.75-1.60 (m, 8H), 1.49-1.29 (m, 10H), 0.90 (t, $^3\text{J}(\text{H-H}) = 6.9$ Hz, 6H)

δ_{C} (100MHz; CD_2Cl_2) 148.81 (dd, $^1\text{J}(\text{C-F}) = 249.5$ Hz, $^2\text{J}(\text{C-F}) = 16.4$ Hz), 143.63 (d, $^2\text{J}(\text{C-F}) = 22.2$ Hz), 132.26 (d, $^3\text{J}(\text{C-F}) = 7.7$ Hz), 129.82 (br s), 129.12 (s), 129.08 (s), 125.18-124.98 (m), 36.00 (s), 35.89 (s), 31.95 (s), 31.67 (s), 31.58 (s), 29.21 (s), 22.96 (s), 14.22 (s)

δ_{F} (376MHz; CD_2Cl_2) -144.17 (s, 2F), -144.16 (s, 2F)

MS (APCI) m/z 741.4 ($\text{M}+\text{H}$)⁺

HRMS : calculated for $\text{C}_{51}\text{H}_{53}\text{F}_4$: 741.4083, found 741.4072

Below: experimental and theoretical isotope pattern

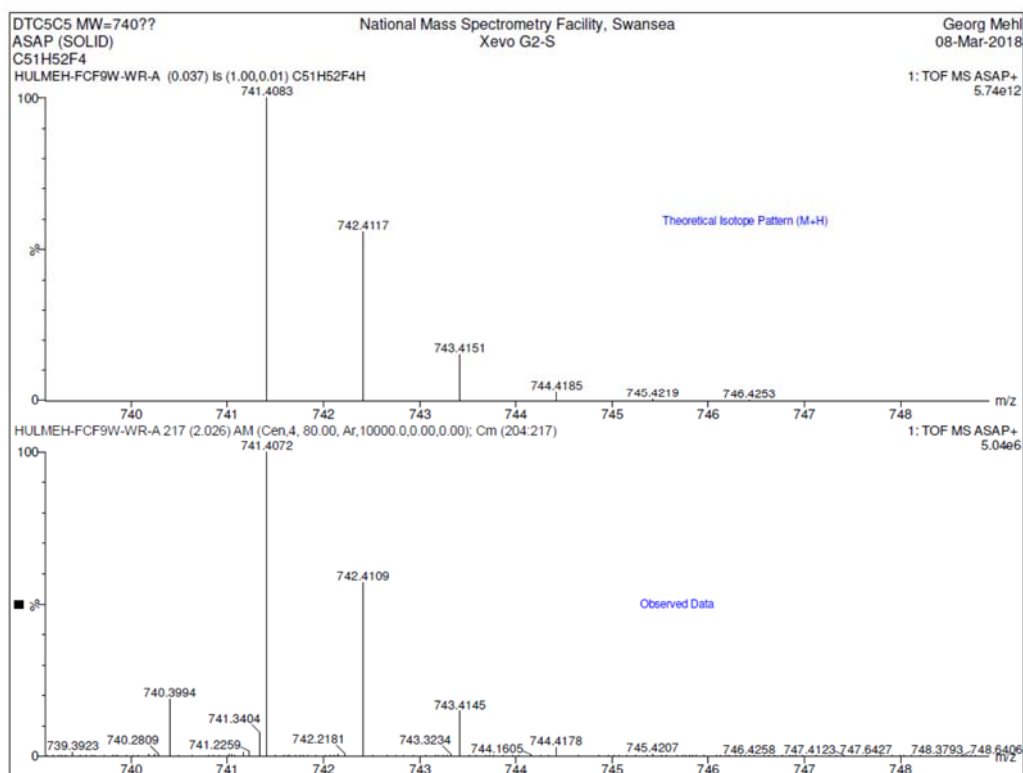
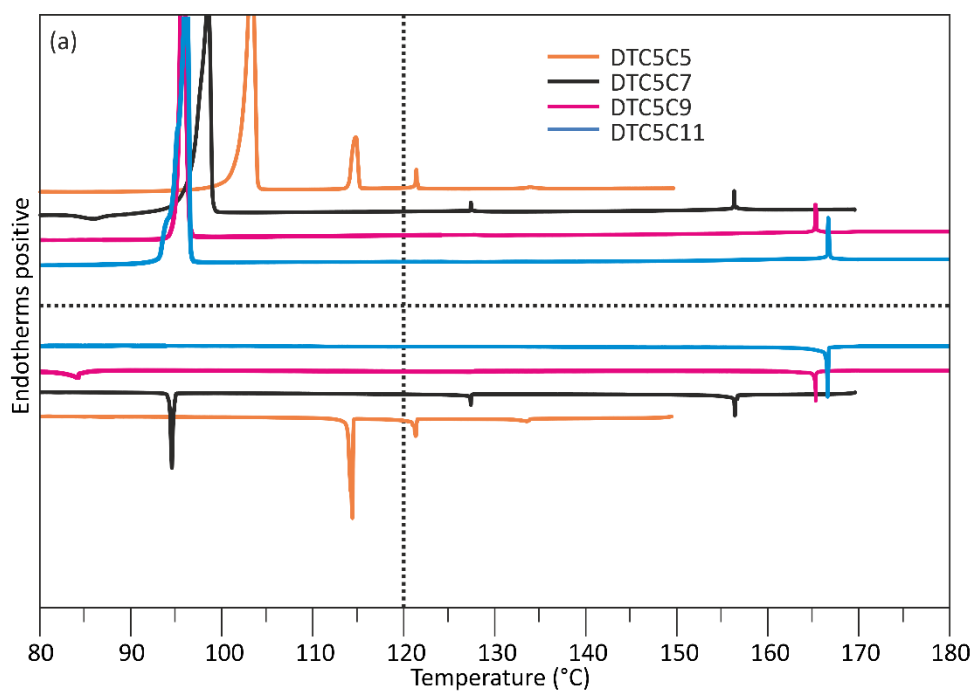


Figure S2 – Experimental and theoretical isotope pattern of DTC5C5.

S2 – Further Standard DSC Data

Standard DSC measurements were recorded using a TA Instruments Q2000 DSC fitted with a cooling unit and a TZero high sensitivity cell. Each of the four DTC5C_n compounds was investigated on heating and cooling using a linear rate of 3 K/min (see Figure S3).



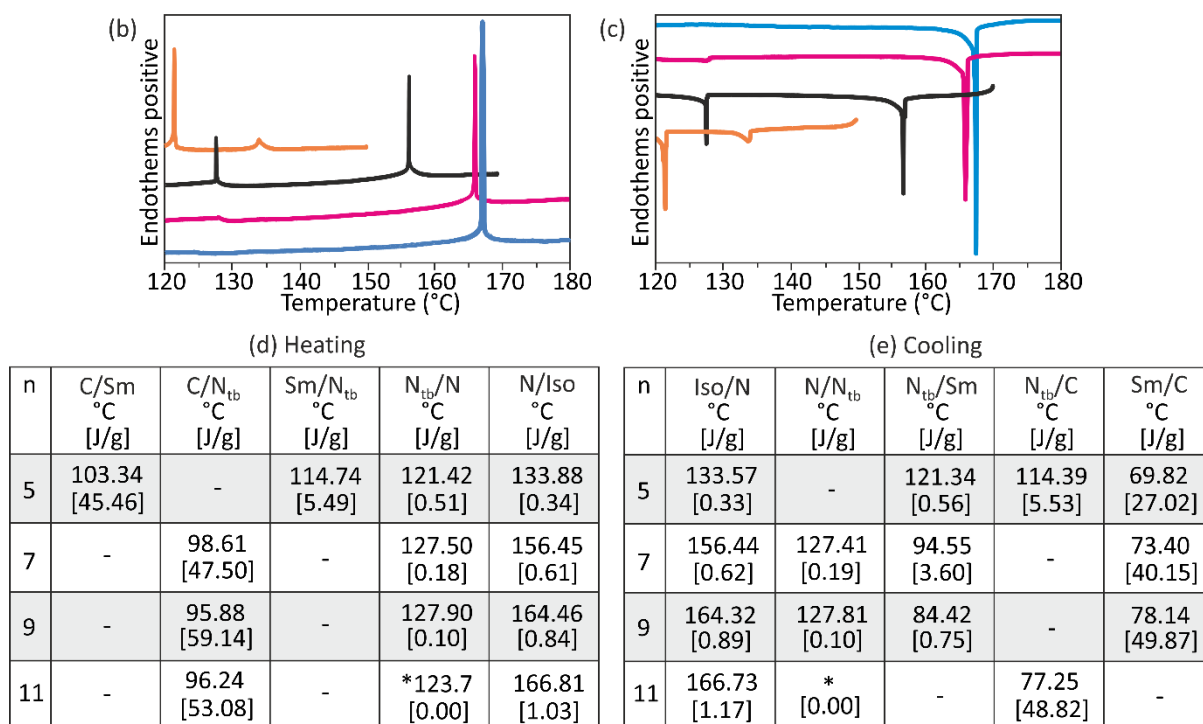
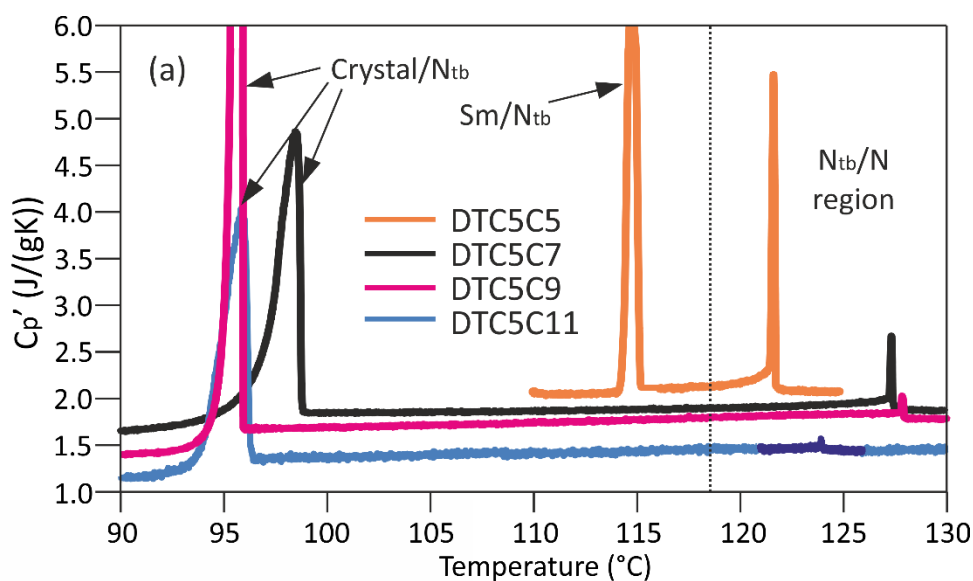


Figure S3 – (a) Linear heating and cooling DSC curves of DTC5C_n compounds at 3 K/min. The region of the N_{tb}/N and N/Iso transitions is magnified in (b) and (c). The colour legend in (a) also applies to (b) and (c). The transition temperatures and measured enthalpies on heating/cooling are tabulated in (d)/(e). *Second order transition; temperature in (d) corresponds to a small hump in C_p' observed using modulated DSC (MDSC).

S3 – Further MDSC Data

Modulated DSC (MDSC) measurements were recorded using a TA Instruments Q2000 DSC fitted with a cooling unit and a TZero high sensitivity cell. The linear heating/cooling rate was $\nu = 0.04$ K/min, but was slowed down in to 0.01K/min in the N_{tb}-N transition region of DTC5C11. The modulation amplitude $\Delta T_M = 0.07$ K, with a frequency $\omega = 0.31$ rad/s (period = 20 s) (see Figure S4).



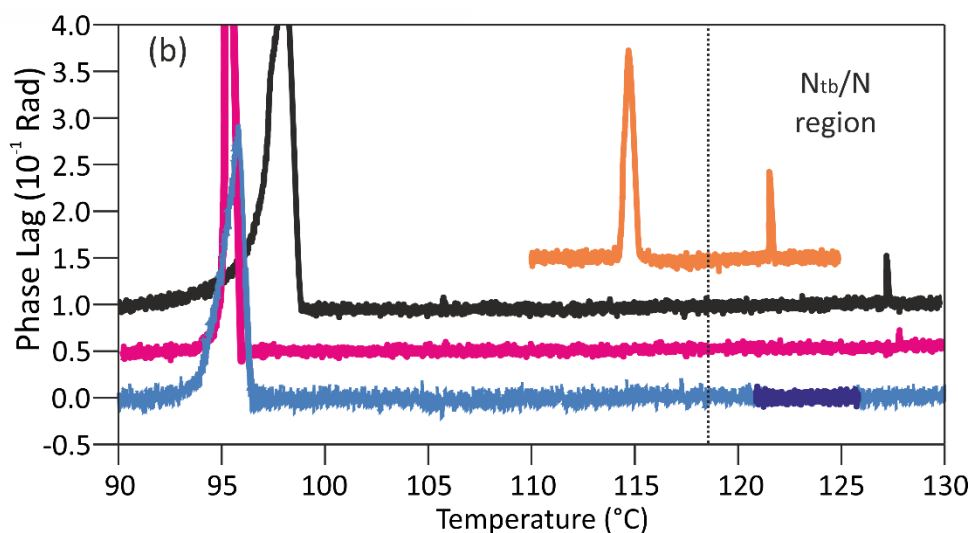


Figure S4 – (a) C_p curves of DTC5C n compounds obtained from MDSC experiments 0.04 K/min. For DTC5C11 the heating rate was slowed down close to the N_{tb}/N transition (121-126 °C) to 0.01K/min. This region is darker blue. (b) Heat flow phase lag curves of DTC5C n compounds. The colour legend and peak labels in (a) also apply to (b).