Supplementary Information

Room-temperature ferroelectric nematic liquid crystal showing a large and divergent density

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SECTION S1 - DSC SCANS

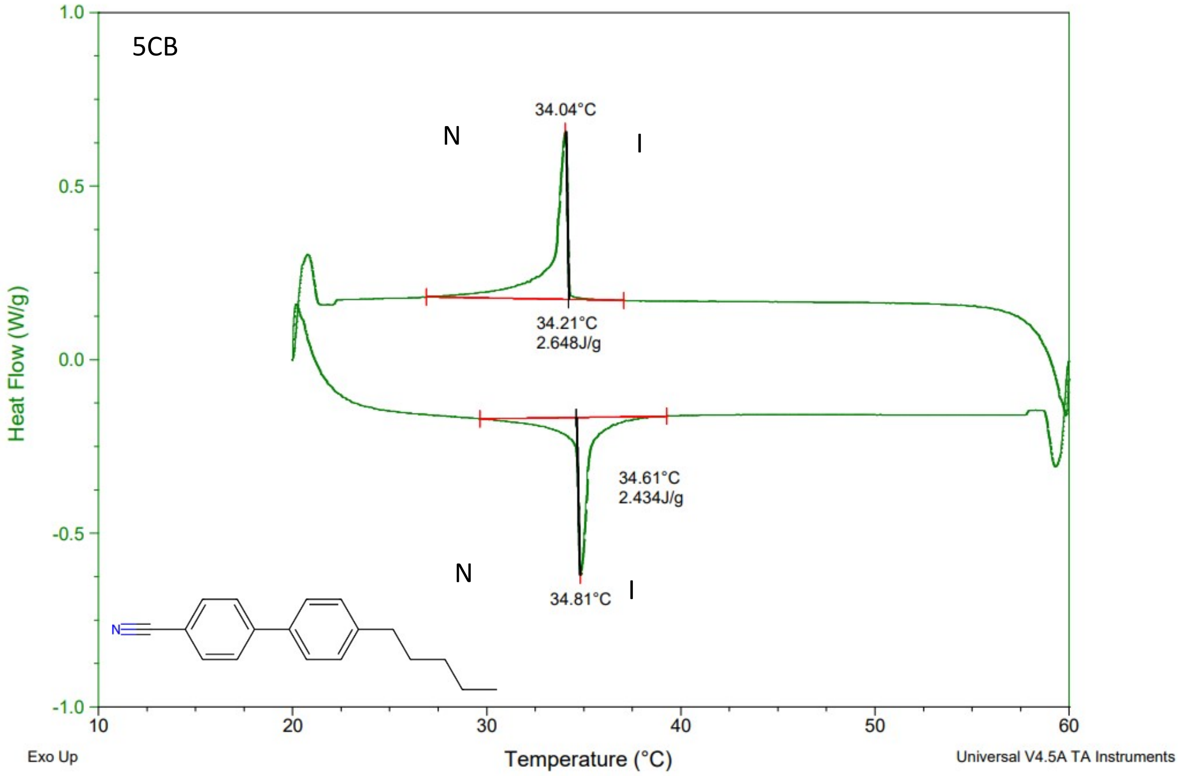


Figure S1: DSC Thermogram (endo up, exo down) for 5CB recorded at (10 dC min^-1). The phase state of liquid crystal through the measurement run is labelled.

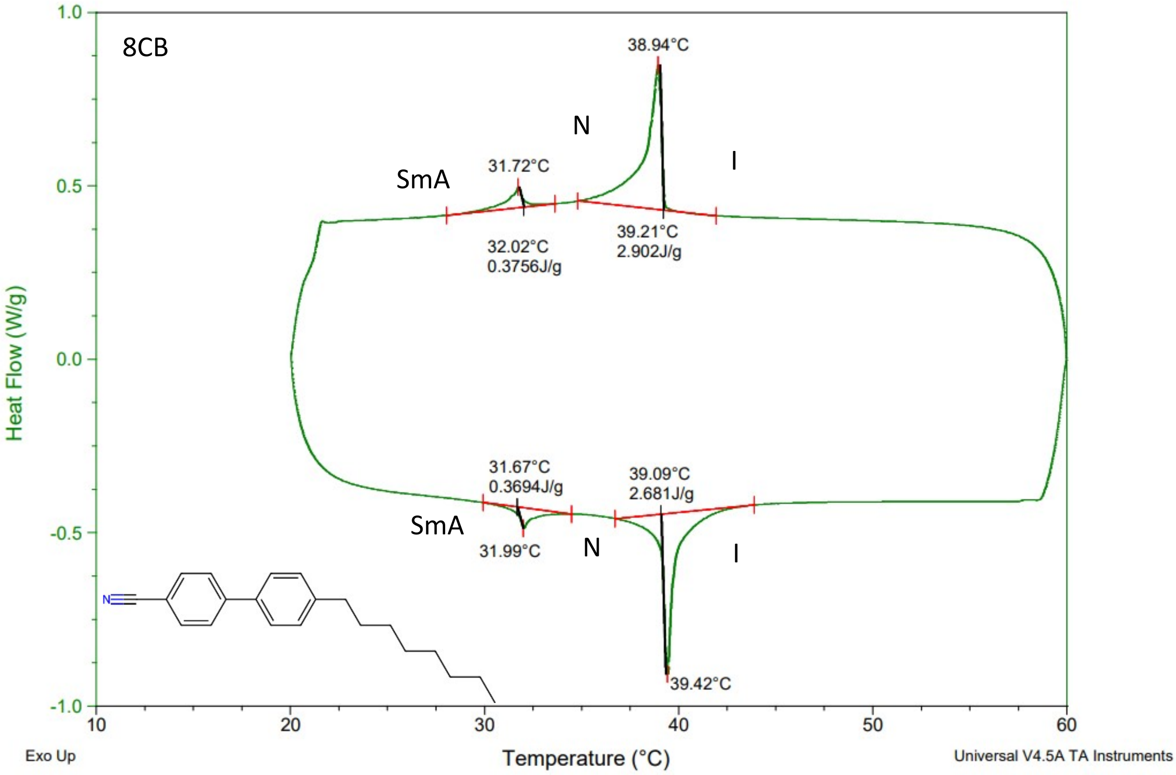


Figure S2: DSC Thermogram (endo up, exo down) for 8CB recorded at (10 dC min^-1). The phase state of liquid crystal through the measurement run is labelled.

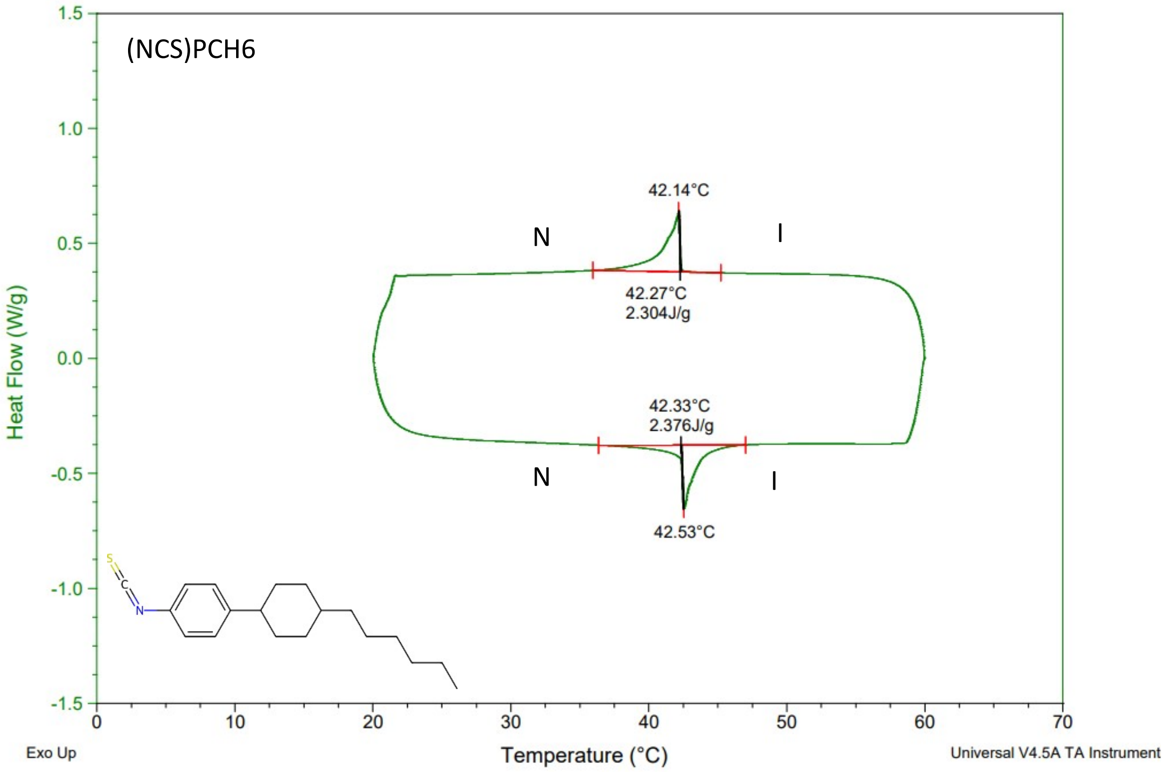


Figure S3: DSC Thermogram (endo up, exo down) for 8CB recorded at (10 dC min^-1). The phase state of liquid crystal through the measurement run is labelled

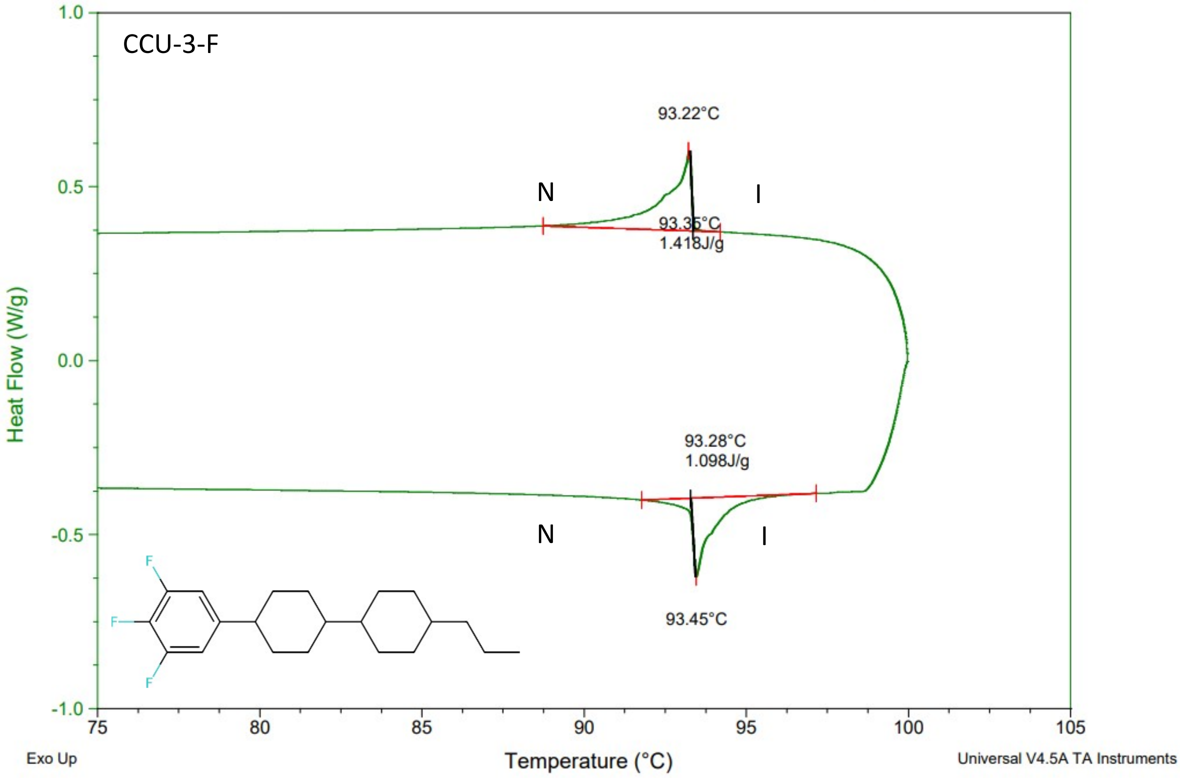


Figure S4. DSC Thermogram (endo up, exo down) for CCU-3-F recorded at (10 dC min^-1). The phase state of liquid crystal through the measurement run is labelled.

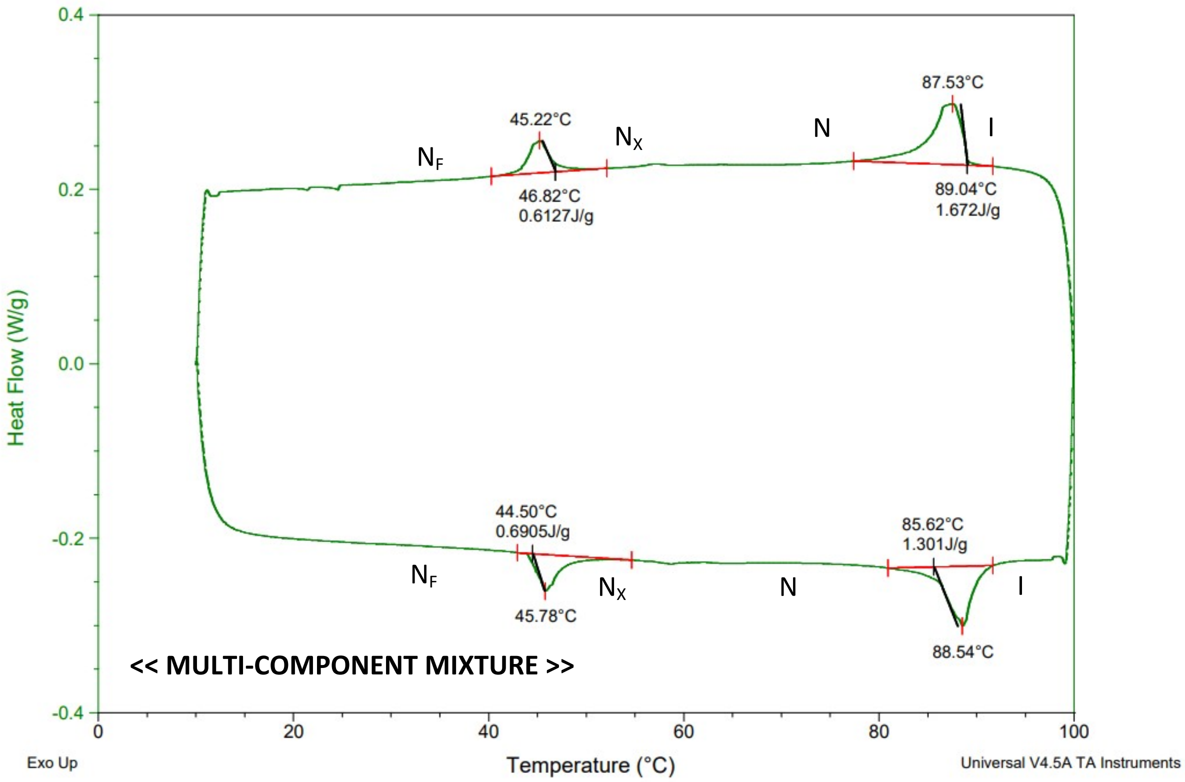


Figure S5. DSC Thermogram (endo up, exo down) for M5 recorded at (10 dC min^-1). The phase state of liquid crystal through the measurement run is labelled.

SECTION S2 - NORMALISED DENSITY DEVIATION EXAMPLE

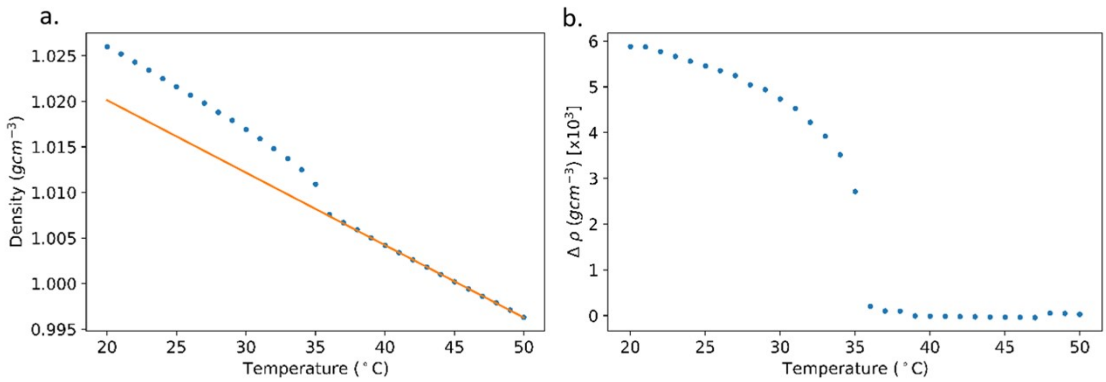


Figure S6. An example to illustrate how the deviation of the density at a transition, $\Delta\rho(T)$ is examined. Densities from a measurement run of 5CB are given in (a) where a linear fit of the density values in the higher temperature phase, $\rho^{highT}(T)$ is also shown. The resulting deviation $\Delta\rho(T) = \rho(T) - \rho^{highT}$ is then shown in (b).

SECTION S3 – DENSITY METER VISCOSITY CORRECTIONS

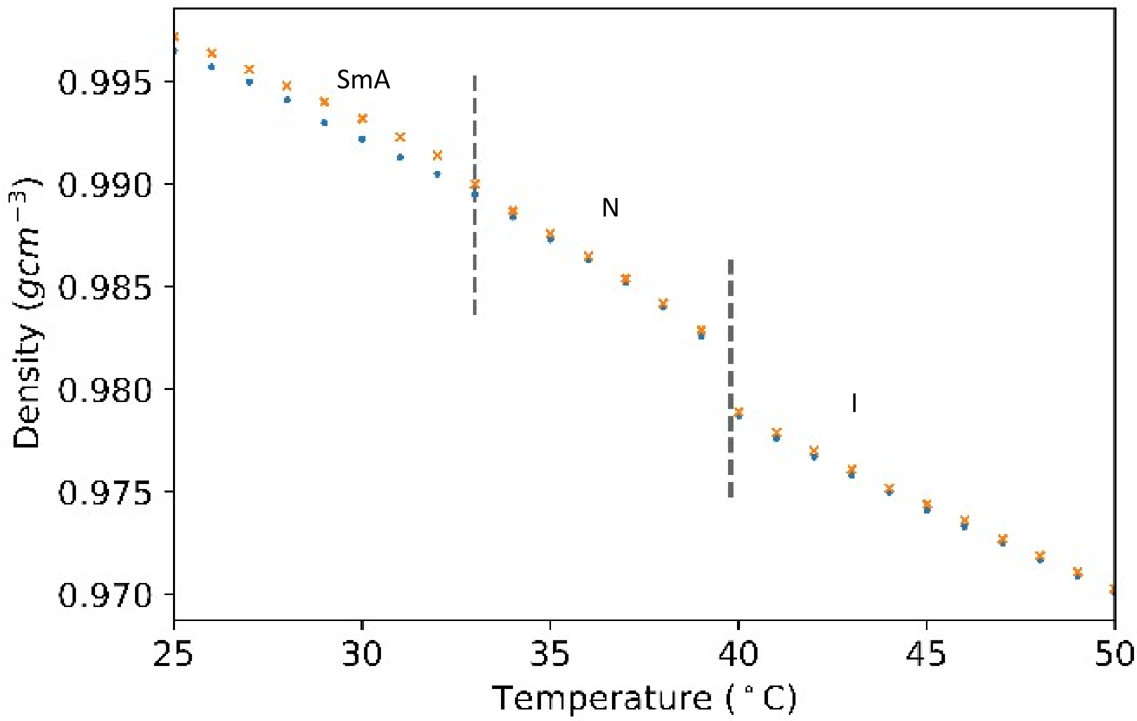


Figure S7. The density, $\rho(T)$ of 8CB. An increased discrepancy between the viscosity corrected (circles) and viscosity non-corrected (crosses) can be seen as 8CB is cooled through SmA-N

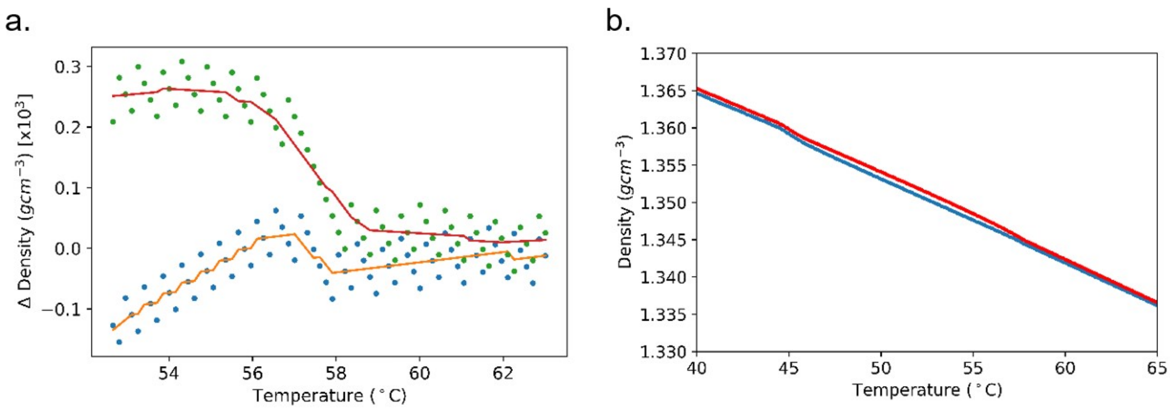


Figure S8. These figures show discounting viscosity corrections for M5 can affect the density values over the (a) N-N_X transition and (b) a temperature range containing N-N_X-N_F phases. In (a) the density data without viscosity corrections are shown as the green dots with the red visual guideline. (b) gives the data without viscosity corrections as the red points.

The N-N_X transition has the smallest $\Delta\rho$ of M5's transitions and does not appear to show any distinct increase in Fig 5. Fig. S8 aims to replicate the visualisation of the I-N and N_X-N_F transitions for N-N_X. The density measurements without viscosity corrections produce a greater deviation at the N_X-N_F which is shown in Fig. S8a. This same procedure can be applied to Fig. 4b to produce a similar plot of the SmA-N transition (Fig. S7). Fig. S8b shows a discrepancy that grows at N-N_X and is maintained through it the N_X phase. It is interesting to note that it decreases at N_F-N_X before growing again on cooling. It should be noted that we do not attempt to make any claims about the viscosity of the liquid crystal material, which is ultimately directional and more complex than this machine can measure, instead we aim to show that there is a damping effect on the oscillating measuring cell that varies through the mesophases.

SECTION S4 - LITERATURE DATA COMPARISONS

LC	Source	Method	Temp range ℃	Resolution ℃	Agreement
5CB	Oweimreen [1]	DMA60 oscillating density meter.	35.0-35.6	0.07>x>0.04	Fig. S9
5CB	Shimada [2]	DA-640 oscillating density meter	19.0-50.0	5.0>x>0.2	Fig. S10
5CB	Zeller [3]	N/A	-10.0 – 50.0	N/A	Fig. S11
5CB	Tintaru [4]	Capillary method	26.5-48.0	2.0>x>0.5	Fig. S12
5CB	Deschamps [5]	Pycnometer	20.0-65.0	13.0 > x > 5.0	Fig. S13
8CB	Oweimreen [6]	DMA60 oscillating density meter	33.56-33.88	0.05 > x > 0.02	Fig. S14
8CB	Dunmur [7]	DMA 02 oscillating density meter	27.0-37.0	10.0	Fig. S15
8CB	Leadbetter [8]	Dilatometer	27.0-50.0	N/A	Fig. S16
(NCS)PCH6	Baran [9]	Pycnometer	23.0-53.0	1.0>x>5.0	Fig. S17

Supplementary Table 1. The available literature data for the selected liquid crystals. The table states the method used to obtain the data, the range over which the data was taken and the minimum and maximum resolution of the data.

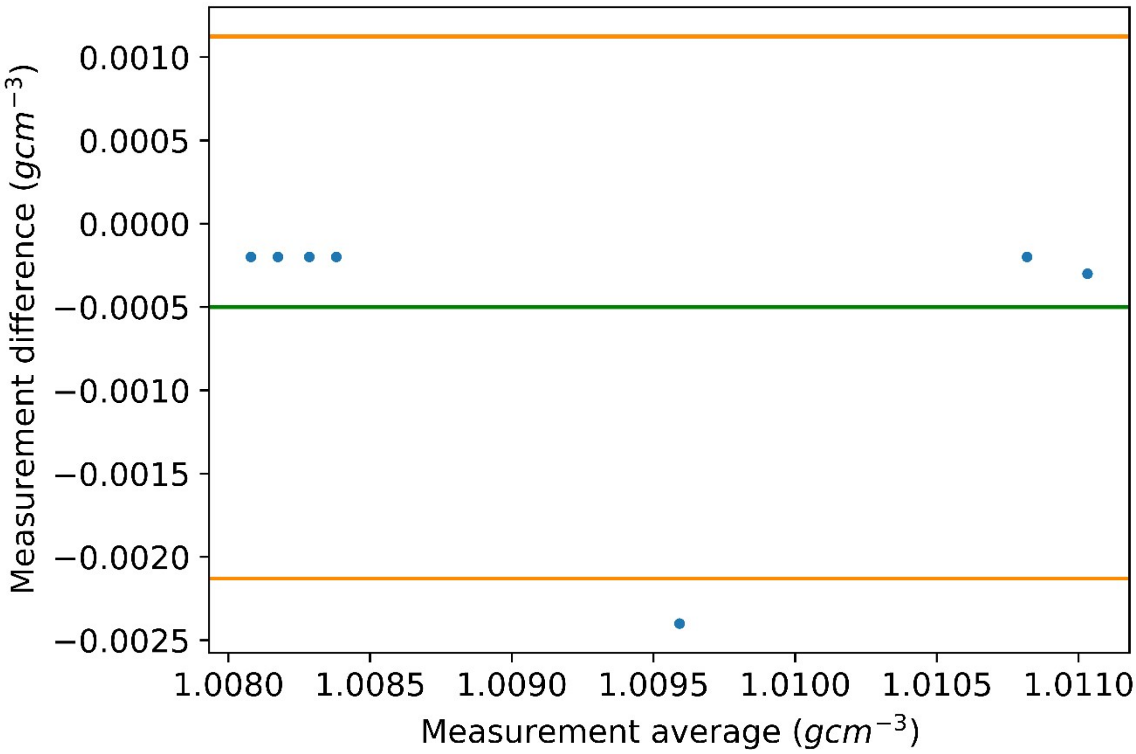


Figure S9. The means of the literature value and measured value are plotted against the difference between the two values (blue points). The orange lines denote the upper and lower bounds of two standard deviations. The green line gives the mean difference between literature and measured values.

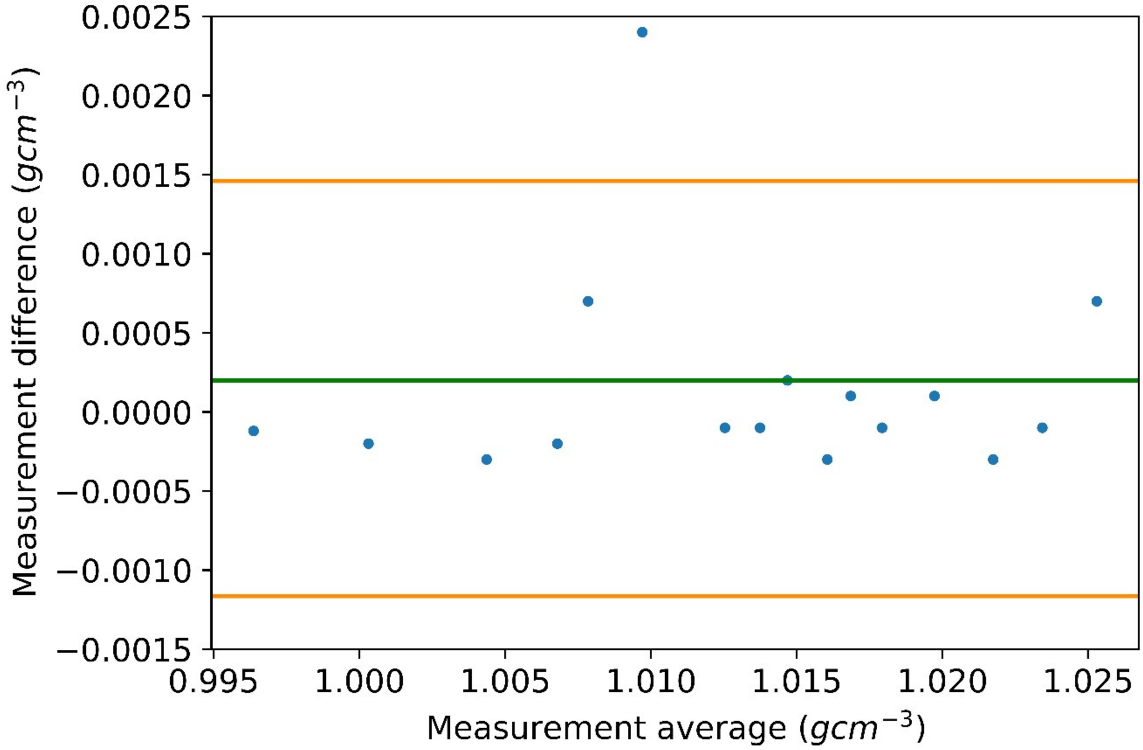


Figure S10. The means of the literature value and measured value are plotted against the difference between the two values (blue points). The orange lines denote the upper and lower bounds of two standard deviations. The green line gives the mean difference between literature and measured values.

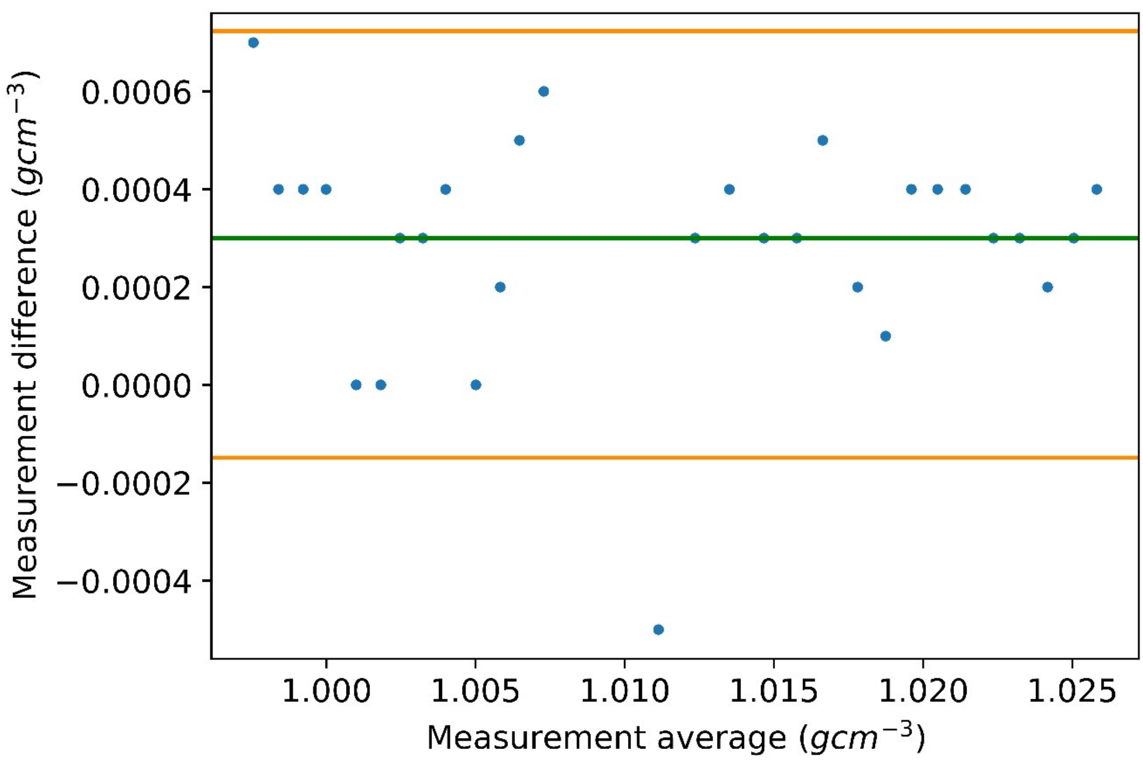


Figure S11. The means of the literature value and measured value are plotted against the difference between the two values (blue points). The orange lines denote the upper and lower bounds of two standard deviations. The green line gives the mean difference between literature and measured values.

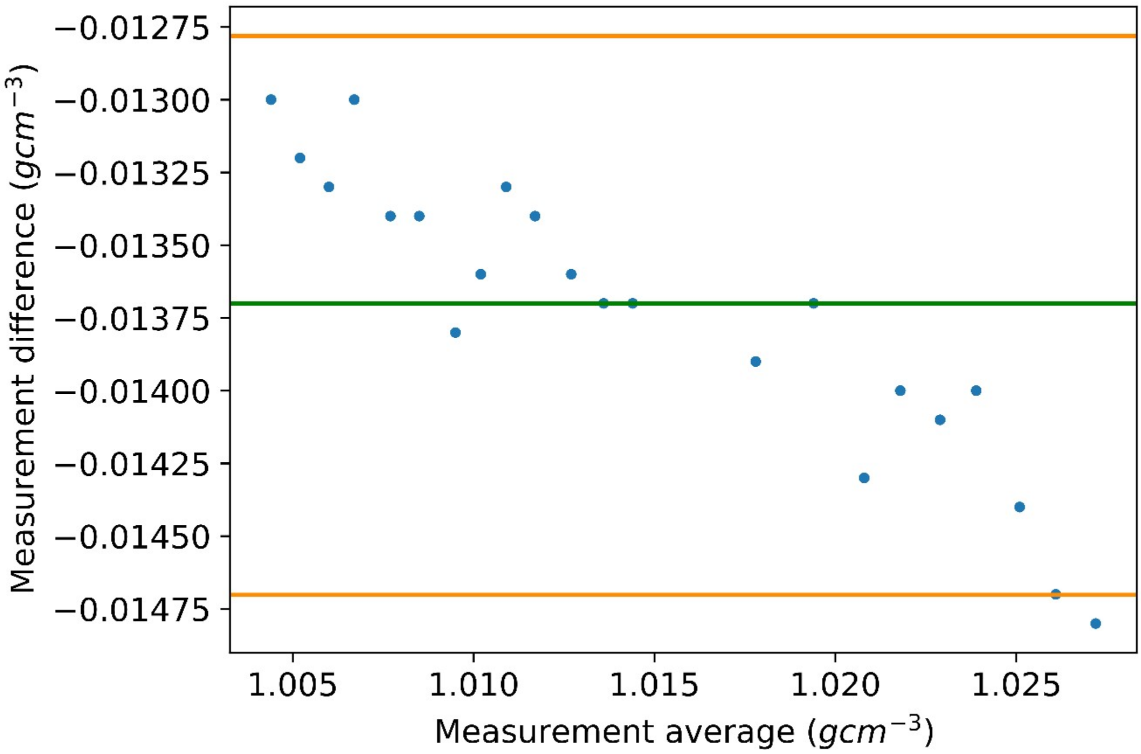


Figure S12. The means of the literature value and measured value are plotted against the difference between the two values (blue points). The orange lines denote the upper and lower bounds of two standard deviations. The green line gives the mean difference between literature and measured values.

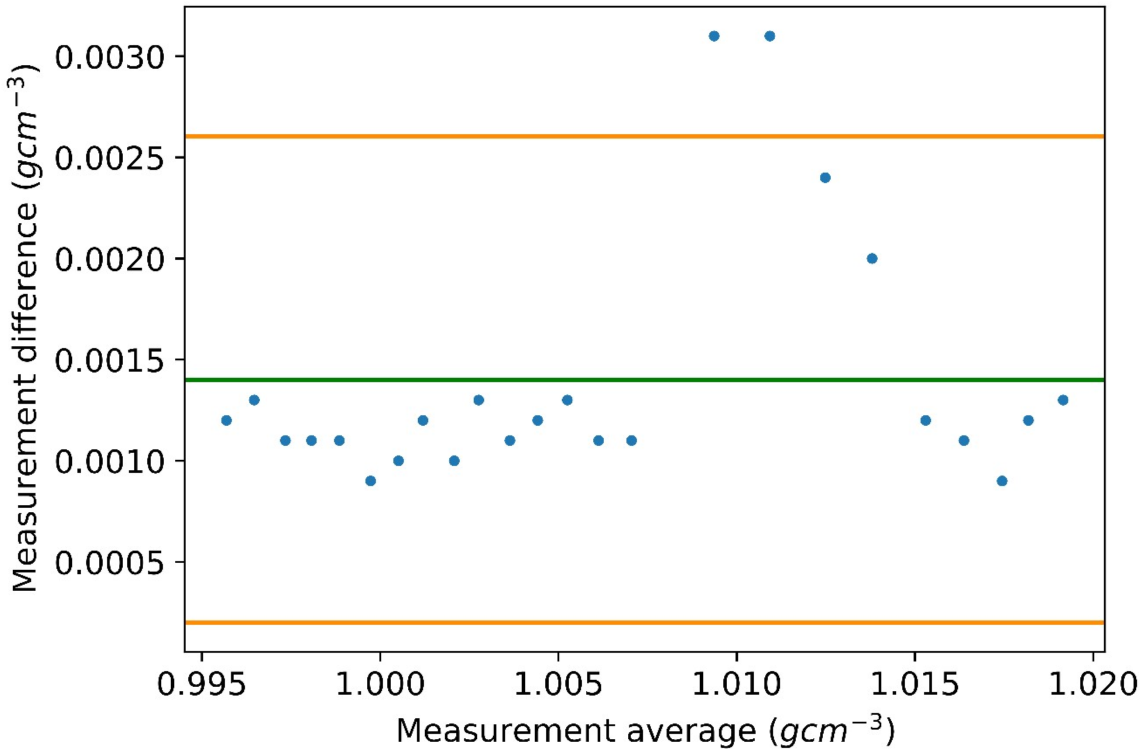


Figure S13. The means of the literature value and measured value are plotted against the difference between the two values (blue points). The orange lines denote the upper and lower bounds of two standard deviations. The green line gives the mean difference between literature and measured values.

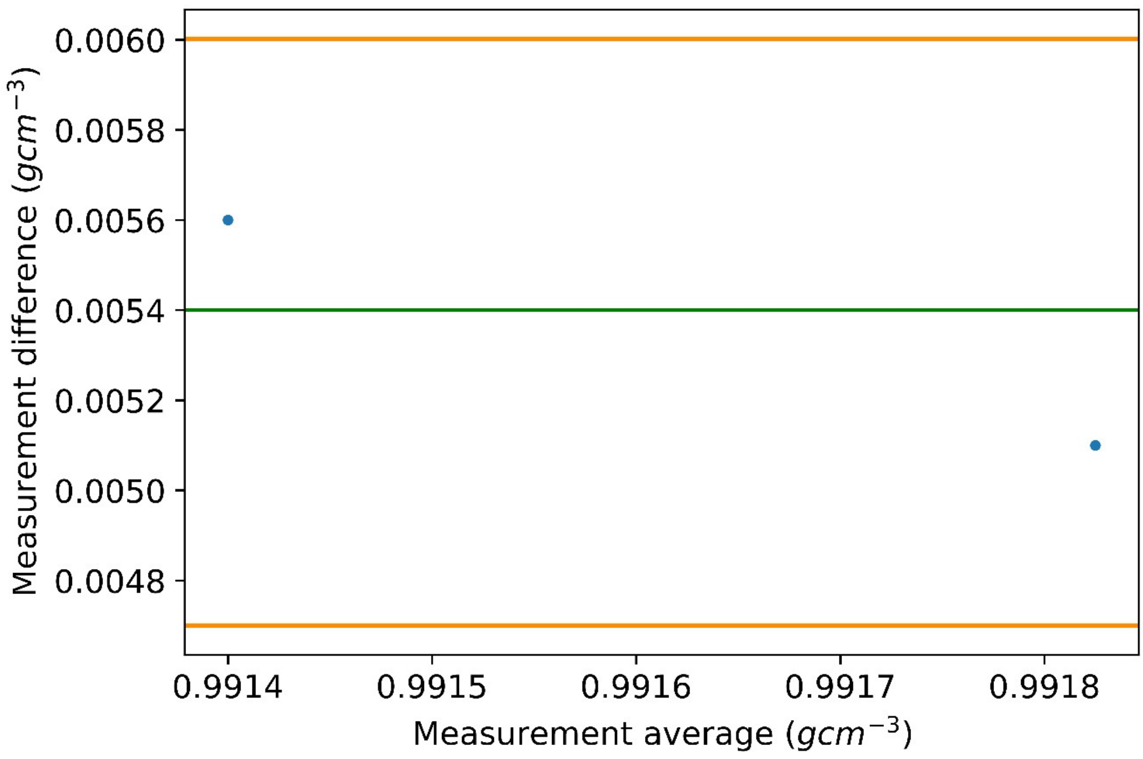


Figure S14. The means of the literature value and measured value are plotted against the difference between the two values (blue points). The orange lines denote the upper and lower bounds of two standard deviations. The green line gives the mean difference between literature and measured values.

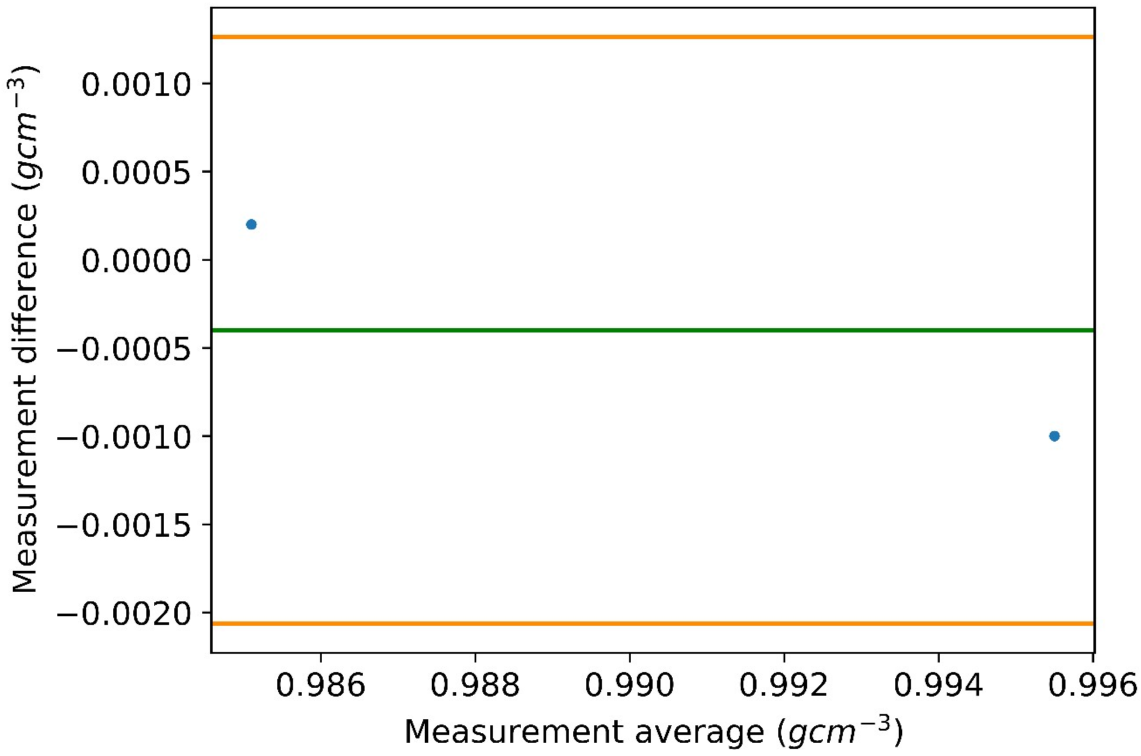


Figure S15. The means of the literature value and measured value are plotted against the difference between the two values (blue points). The orange lines denote the upper and lower bounds of two standard deviations. The green line gives the mean difference between literature and measured values.

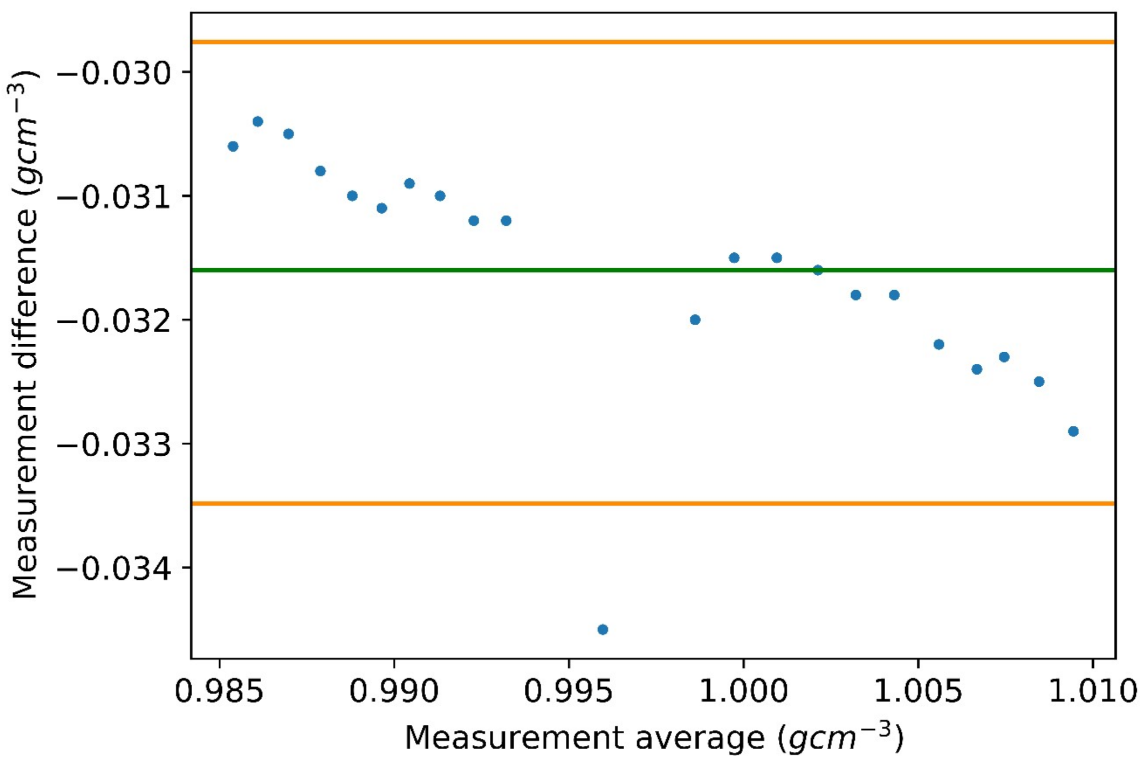


Figure S16. The means of the literature value and measured value are plotted against the difference between the two values (blue points). The orange lines denote the upper and lower bounds of two standard deviations. The green line gives the mean difference between literature and measured values.

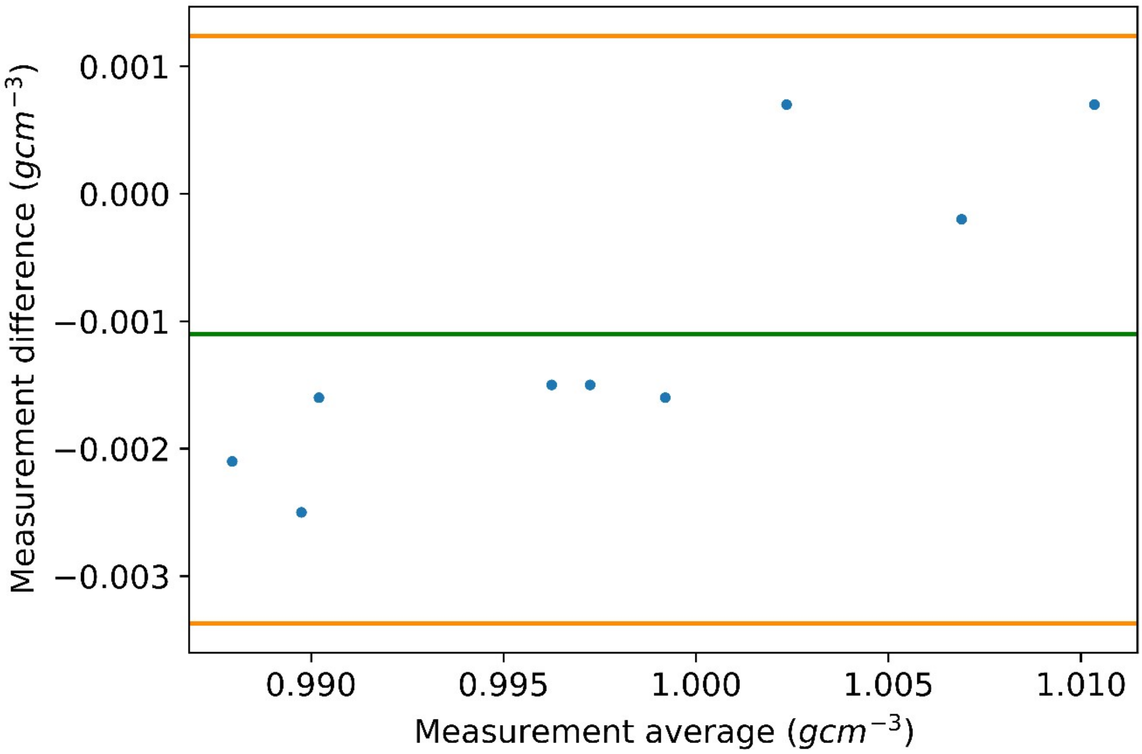


Figure S17. The means of the literature value and measured value are plotted against the difference between the two values (blue points). The orange lines denote the upper and lower bounds of two standard deviations. The green line gives the mean difference between literature and measured values.

SECTION S5 – TEMPERATURE DEPENDENT DENSITY BEHAVIOUR

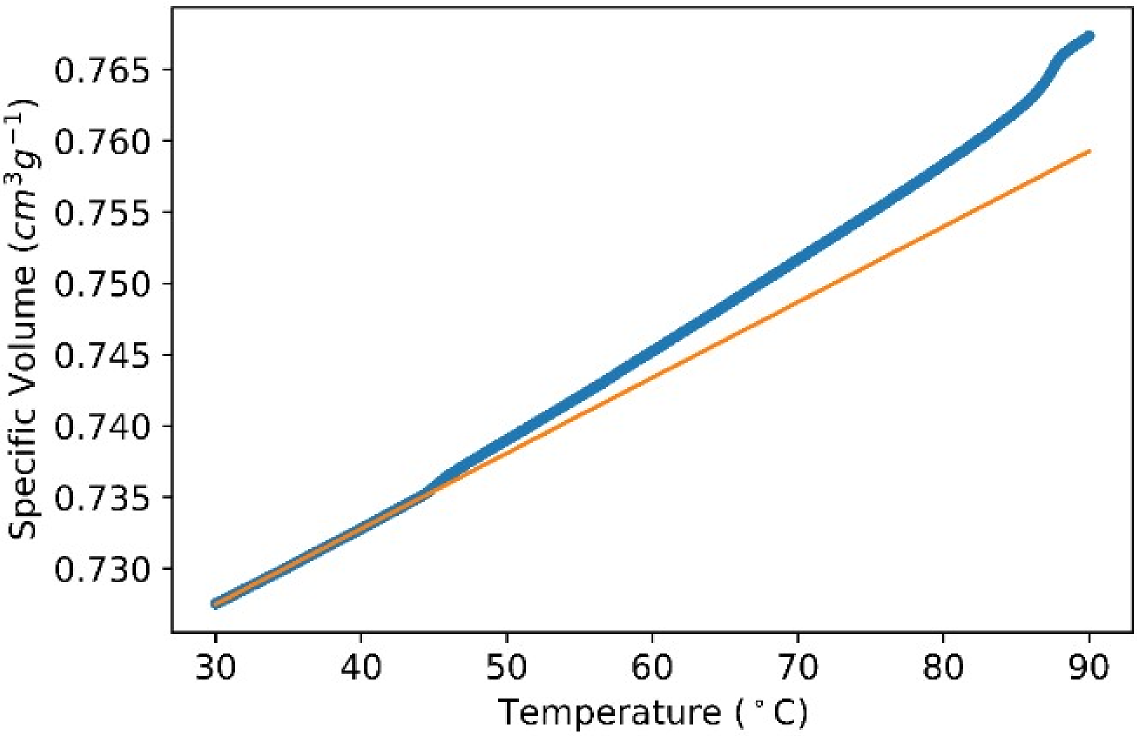


Figure S18. The specific volume (1/density) of M5. The orange line represents the linear fit of the density data that is used to calculate a value for the expansion coefficient, α

The calculated expansion coefficients, α, vary through the phases for every material (table 1). The density data provides different values for the expansion coefficient of N and N_X in M5 as well as the SmA and N phases in 8CB. These correspond to phases in which their transitions do not produce clear deviations. This provides an alternative method for identifying the phase transition through analysis of the specific volume's gradient.

Using our DSC data (SI section 1), a loose correlation between the transition enthalpies and the density increases, $\Delta\rho$ can be observed. There will also be a contribution to the density increase from the expansion coefficient with the larger values adding a larger increase to the volume over the transition. M5 differs from the selected materials as it is a mixture. Possibly due to this the transitional enthalpy and density increase of M5 does not follow the correlations of the single component materials. Its larger N-I density increase (Fig 6. (b), supplementary table 2) is a result of the transition density increase taking place over a larger temperature range ($\approx$ 1.5K vs. $\approx$ 0.5K) than the conventional material. However, its transitional enthalpy is closest to that of CCU-3-F and smaller than the other materials.

Material	**Transition Enthalpies** (J/g)	$\Delta\rho 10^3$ (g/cm^3)
M5	1.424	3.1
5CB	2.648	2.2
8CB	2.902	2.5
CCU-3-F	1.418	1.9
(NCS)PCH6	2.304	2.8

Supplementary Table 2. A comparison between the transition enthalpies and density deviations of the I-N transitions for the LC materials. There appears to be a loose relationship between the size of the transition enthalpies and the magnitude of the density deviation for the selected materials. This does not hold true for the multi-component M5.

We have noted that considering the contribution of the viscosity to the corrections made by the density meter can allow for the graphical observation of transitions. The viscosity behaviour of liquid crystals is highly complex and outside the scope of this work. However, it is an interesting parallel that the viscosity correction occurs in both 8CB and M5. If we assume that there is some increase in the viscosity of M5 at N_X-N (like that of SmA-N of 8CB) then the discrepancy between the corrected and uncorrected density values can potentially be understood. This is a logical direction to be explored in future work.

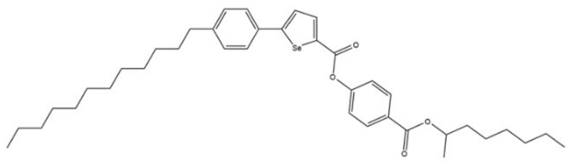
SECTION S6 – FERROELECTRICS STRUCTURES AND PHASE SEQUENCES

a.

<< Multi-Component Mixture >>

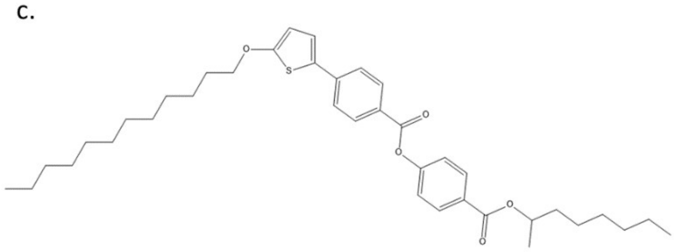
SCE8: Iso 100 N* 79 A 59 SmC*

b.



1: Iso 116.6 SmA 109.4 SmC* 99.0 SmC*$_{FI1}$ 97.8 SmC*$_{A}$

c.



2: Iso 96.8 SmA 87.6 SmC*$_{a}$ 85.8 SmC* 82.8 SmC*$_{FI1}$ 80.3 SmC*$_{A}$

Figure S19. Phase sequences and molecular structures (where applicable) of a) SC8 and compound b) **1** and c) **3** [10, 11].

1. Oweimreen, G.A., et al., *Density Measurements in the Nematic and Isotropic Phases of 5CB and Dilute Solutions of Tetraethylmethane in 5CB.* Molecular Crystals and Liquid Crystals, 1986. **138**(1): p. 327-338.
2. Shimada, R. and H. Watanabe, *Thermodynamic Effect on Viscosity and Density of a Mixture of 4-Cyano-4 '-pentylbiphenyl (5CB) with Dilute Dimethyl Phthalate (DMP).* Nihon Reoroji Gakkaishi, 2020. **48**(4): p. 199-206.
3. Zeller, H.R., *Dielectric relaxation in nematics and Doolittle's law.* Physical Review A, 1982. **26**(3): p. 1785-1787.
4. Tintaru, M., et al., *Surface tension of some liquid crystals in the cyanobiphenyl series.* Liquid Crystals, 2001. **28**(5): p. 793-797.
5. Deschamps, J., J.P.M. Trusler, and G. Jackson, *Vapor Pressure and Density of Thermotropic Liquid Crystals: MBBA, 5CB, and Novel Fluorinated Mesogens.* The Journal of Physical Chemistry B, 2008. **112**(13): p. 3918-3926.
6. Oweimreen, G.A., *On the Nature of the Smectic A-to-Nematic Phase Transition of 8CB.* The Journal of Physical Chemistry B, 2001. **105**(35): p. 8417-8419.
7. Dunmur, D.A., et al., *The Dielectric and Optical Properties of the Homologous Series of Cyano-Alkyl-Biphenyl Liquid Crystals.* Molecular Crystals and Liquid Crystals, 1978. **45**(1-2): p. 127-144.
8. Leadbetter, A.J., J.L.A. Durrant, and M. Rugman, *The Density Of 4 n-Octyl-4-Cyano-Biphenyl (8CB).* Molecular Crystals and Liquid Crystals, 1976. **34**(10): p. 231-235.

9. Baran, W., et al., *Some Physical Properties of Mesogenic 4-(trans-4'-n-Alkylcyclohexyl) Isothiocyanatobenzenes.* Molecular Crystals and Liquid Crystals, 1985. **123**(1): p. 237-245.
10. Mills, J., et al., *The physical properties of a series of antiferroelectric hetrocyclic esters.* Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 1997. **303**(1): p. 145-152.
11. Roberts, N.W., et al., *An experimental and theoretical investigation into the reflection spectra of SmC* and SmC A* phases.* Journal of Materials Chemistry, 2003. **13**(2): p. 353-359.