Supporting Information

Insights into the Nanostructuring and Phase Behaviour of an All-Aromatic Prototypical Nematic Liquid Crystal

Henry Adenusi[1*], Luca Muccioli[2], Matteo Lanciotti[1], Maruti Hegde[3], Theo J. Dingemans[3], Edward T. Samulski[3], Francesco Vita[1], Oriano Francescangeli[1*]

[1]Department of Science and Engineering of Materials, Environment and Urban Planning, Marche Polytechnic University, Via Brecce Bianche, 60131, Ancona, Italy

[2]Department of Industrial Chemistry, University of Bologna, Via Gobetti 85, 40129, Bologna, Italy

[3]Department of Applied Physical Sciences, University of North Carolina at Chapel Hill, Murray Hall, 121 South Road, Chapel Hill, NC 27599-3050, USA.

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TOPOLOGY FILE (CHARMM FORMAT)

AUTOgenerate ANGLES DIHEDRAL

MASS 1 CA 12.0110 CA
MASS 2 CP 12.0110 CP
MASS 3 HA 1.0079 HA

RESIDUE PNP 0.0
b3lyp/6-311++g(d,p) Pop=Espdipole charges, symmetrized

group
atom C1 CA -0.160075
atom H2 HA +0.130800
atom C3 CA -0.126375
atom H4 HA +0.128200
atom C5 CA -0.139550
atom H6 HA +0.131100
atom C7 CA -0.126375
atom H8 HA +0.128200
atom C9 CA -0.160075
atom H10 HA +0.130800
atom C11 CP +0.050100
atom C12 CP +0.084400
atom C13 CA -0.199800
atom C14 CA -0.094600
atom H15 HA +0.121100
atom H16 HA +0.135550
atom C17 CA -0.199800
atom H18 HA +0.135550
atom C19 CA -0.094600
atom H20 HA +0.121100
atom C21 CP -0.015050
atom C22 CP +0.073900
atom C23 CA -0.312050
atom H24 HA +0.166000
atom C25 CA -0.140650
atom H26 HA +0.138800
atom C27 CA -0.329000
atom H28 HA +0.180100
atom C29 CA +0.242300
atom C30 CA -0.312050
atom H31 HA +0.166000
atom C32 CA +0.242300
atom C33 CA -0.329000
atom H34 HA +0.180100
atom C35 CA -0.140650
atom H36 HA +0.138800
atom C37 CP +0.073900
atom C38 CP -0.015050

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atom  C39    CA   -0.094600
atom  C40    CA   -0.199800
atom  H41    HA   +0.135550
atom  H42    HA   +0.121100
atom  C43    CA   -0.094600
atom  H44    HA   +0.121100
atom  C45    CA   -0.199800
atom  H46    HA   +0.135550
atom  C47    CP   +0.084400
atom  C48    CP   +0.050100
atom  C49    CA   -0.160075
atom  H50    HA   +0.130800
atom  C51    CA   -0.126375
atom  H52    HA   +0.128200
atom  C53    CA   -0.139550
atom  H54    HA   +0.131100
atom  C55    CA   -0.126375
atom  H56    HA   +0.128200
atom  C57    CA   -0.160075
atom  H58    HA   +0.130800

bond C1    H2
bond C1    C3
bond C1    C11
bond C3    H4
bond C3    C5
bond C5    H6
bond C5    C7
bond C7    H8
bond C7    C9
bond C9    H10
bond C9    C11
bond C11   C12
bond C12   C13
bond C12   C17
bond C13   C14
bond C13   H16
bond C14   H15
bond C14   C21
bond C17   H18
bond C17   C19
bond C19   H20
bond C19   C21
bond C21   C22
bond C22   C23
bond C22   C25
bond C23   H24
bond C23   C32
bond C25   H26
bond C25   C27
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bond C27 H28
bond C27 C29
bond C29 C30
bond C29 C32
bond C30 H31
bond C30 C37
bond C32 C33
bond C33 H34
bond C33 C35
bond C35 H36
bond C35 C37
bond C37 C38
bond C38 C39
bond C38 C43
bond C39 C40
bond C39 H42
bond C40 H41
bond C40 C47
bond C43 H44
bond C43 C45
bond C45 H46
bond C45 C47
bond C47 C48
bond C48 C49
bond C48 C57
bond C49 H50
bond C49 C51
bond C51 H52
bond C51 C53
bond C53 H54
bond C53 C55
bond C55 H56
bond C55 C57
bond C57 H58

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ADDITIONAL DATA

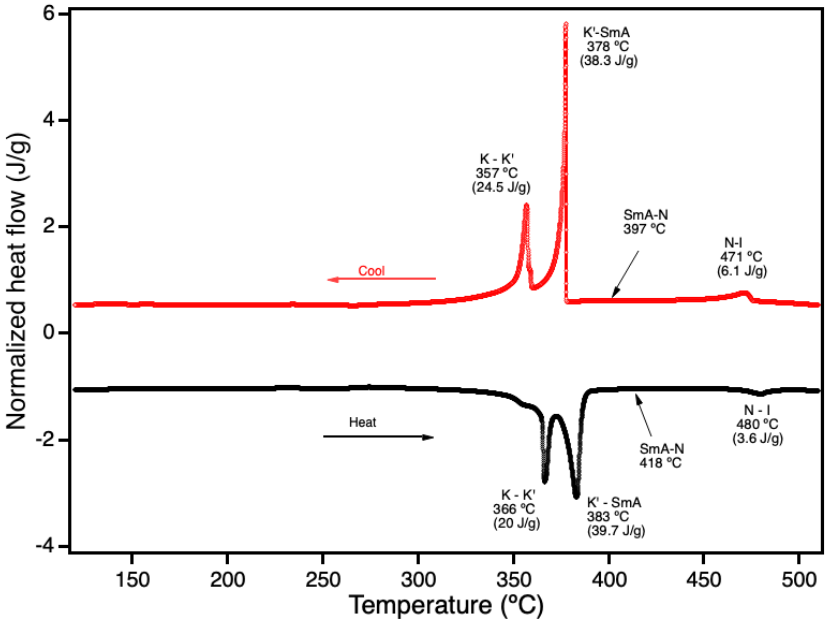

Figure S1: DSC data collected on the 2nd cycle (heating-cooling rate: 20 K/min).

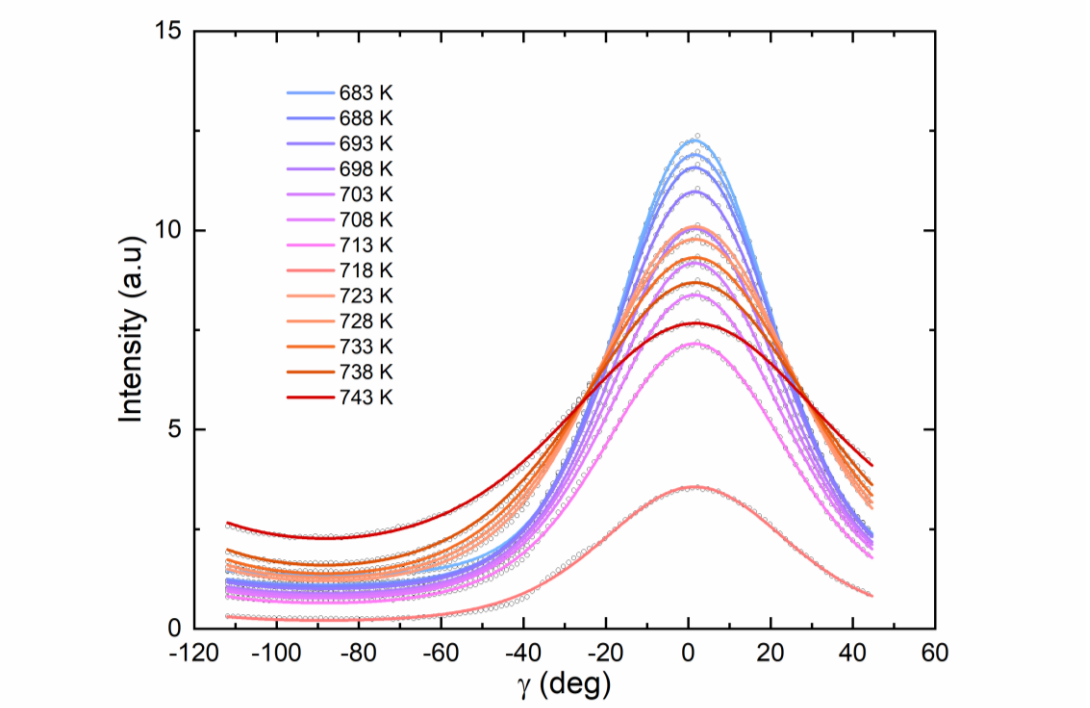

Figure S2: Azimuthal intensity profiles of the XRD wide-angle features at different temperatures across the nematic phase (empty circles) and best fit curves computed using the model described in the article (solid lines).

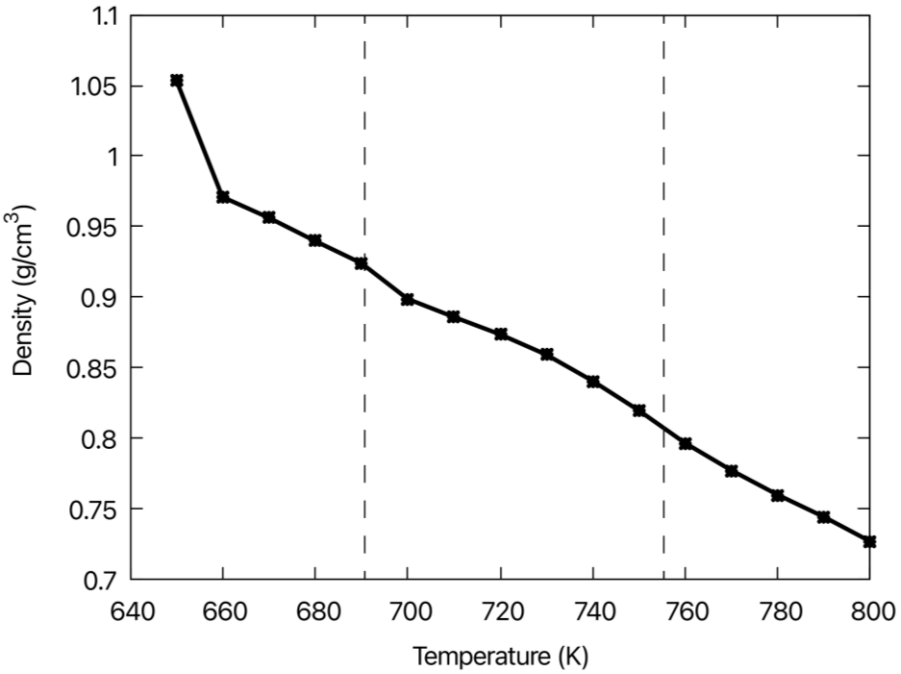

Figure S3: Simulated mass density as a function of temperature for PPNPP. The vertical dashed lines indicate the calculated transition temperatures from the MD simulations.

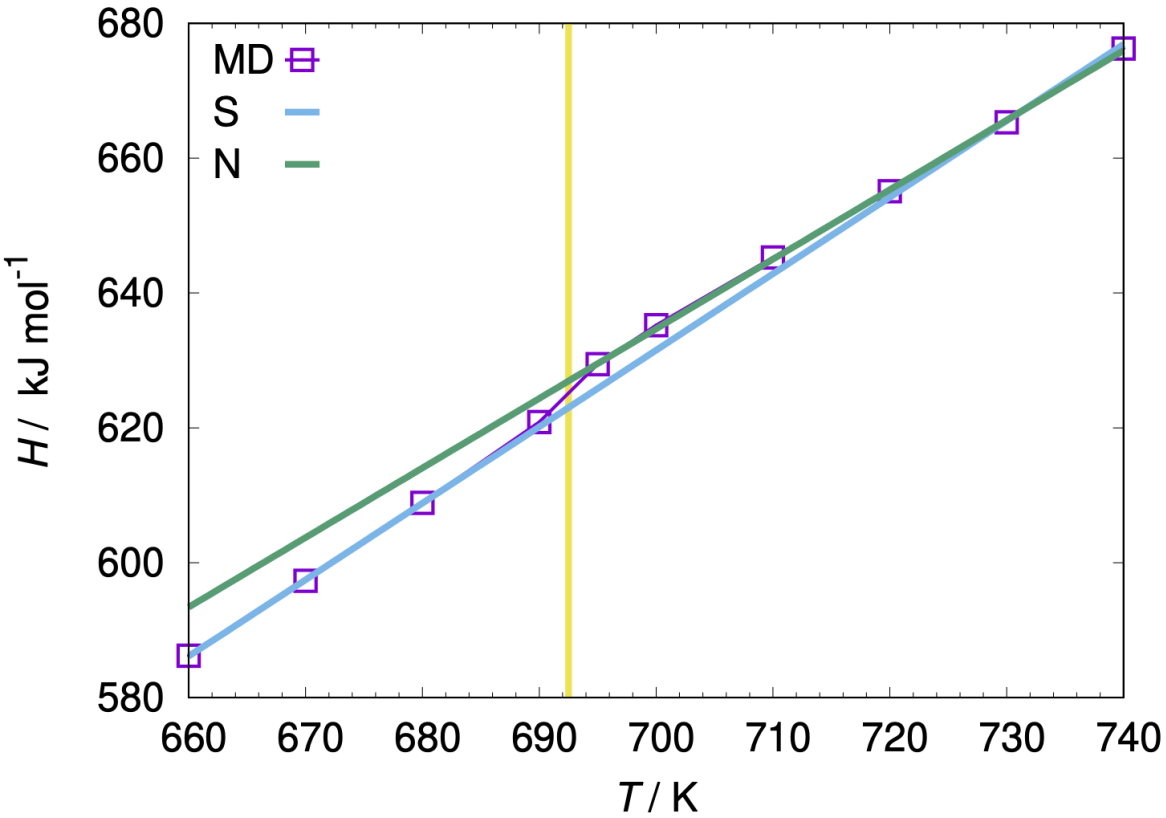

Figure S4: Simulated enthalpies H as a function of temperature T for PPNPP (purple squares) with the determined $T_{SmA\text{-}N}$ transition at 692.5 K (yellow line). The green and blue lines show the different linear trend of $H(T)$ in the nematic and smectic A temperature range, respectively.

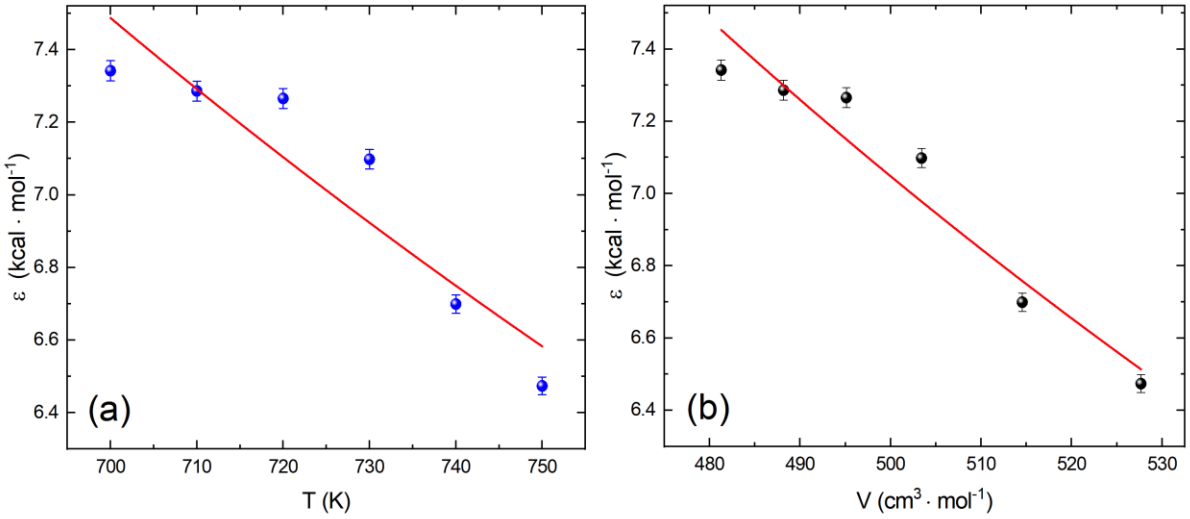

Figure S5. (a) ε values, obtained by fitting the orientational energies with the model $U(\cos\theta) = U_0 - \varepsilon[< P_2 > P_2(\cos\theta) + \lambda < P_4 > P_4(\cos\theta)]$, reported as a function of the temperature and their best fit with a power law curve; (b) the same values of ε reported as a function of the molar volume V and their fit with a power law curve. The values of V are computed from the density data in Figure S2. The value of ε at 695 K has been omitted in the fits because too close to the transition. The fit results are reported in the paper.