Supplementary Information to

Dipole-dipole correlations in the nematic phases of symmetric cyanobiphenyl dimers and their binary mixtures with 5CB

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I. POM textures and temperature dependence of dielectric permittivity
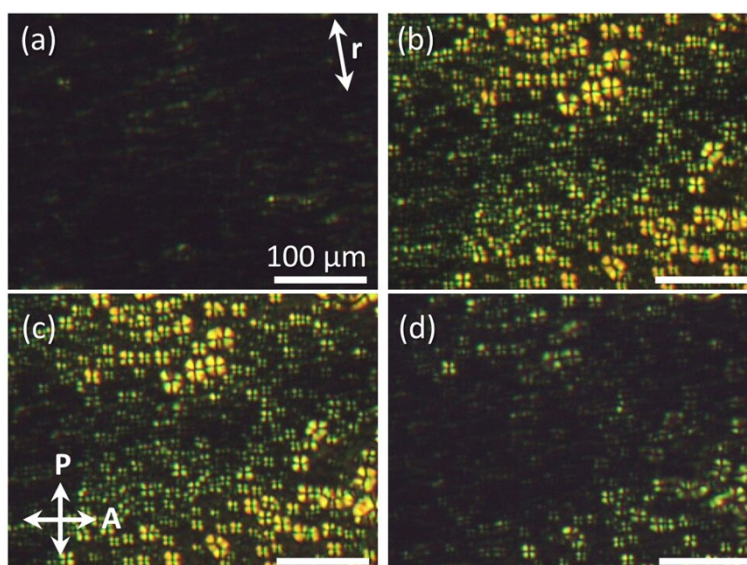

Figure SI1. *Optical textures of the N_x phase obtained during POM observations following Protocol 2 (see main text); Cooling in the presence of 25 V_{rms} at (a) 70.5°C and (b) 48°C and subsequent heating after field removal at (c) 58.3°C and (d) 70.5°C.*
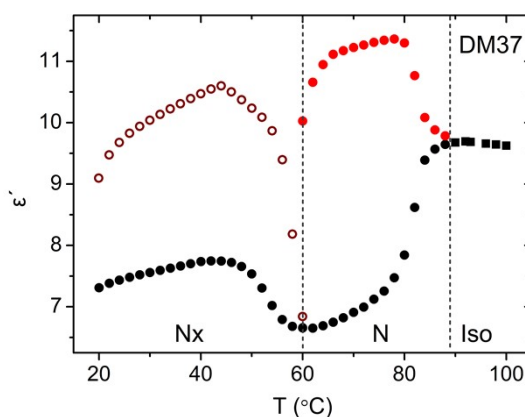

Figure SI2. *Temperature dependence of dielectric permittivity at f = 5 kHz of DM37. Squares-ε_{iso}; Black circles-$\varepsilon_\perp$; Red circles-$\varepsilon_\parallel$ measured with P.1; Open circles–$\varepsilon_\parallel$ measured with P.2. The progressive loss of homeotropic alignment achieved with Protocol 2 is observed on heating towards the N phase.*

II. Conformational statistics of the dimer molecules and *intra*-molecular correlations

The conformational properties of a single isolated symmetric dimer are associated with the potential $E(n;\hat{L}_1,\hat{L}_2)$, which takes into account both bonded and non-bonded intramolecular interactions. Here n defines the molecular conformation, or, equivalently, describes a conformational state through the necessary internal degrees of freedom of the linear flexible spacer, i.e. torsion and bond angles, bond lengths etc., and $\hat{L}_1,\hat{L}_2$ correspond to the conformation dependent orientations of the rigid mesogenic cores which are assumed cylindrically symmetric, see inset in Figure SI3.

The temperature dependent probability density, $p(c) = \langle \delta(c - \hat{L}_1 \cdot \hat{L}_2) \rangle_{conf}$, i.e. the probability to find the rigid cores of a single isolated dimer forming an angle θ_{12} with $cos\theta_{12} = c$, is of central importance for the study of orientational dependent properties in the nematic state. In this work we have modelled, $p(c)$, as $p(c) = \zeta \exp[-\beta E(c)]$ where $\beta = 1/k_B T$, ζ the normalization constant and $E(c)$ an effective internal energy of the dimer as a function of the relative orientation of the cores. Formally, $E(c)$ can be represented as a Legendre polynomial series

$$E(c) = \sum_{i=0}^{\infty} a_l P_l(c)$$

with a clear dependence of the expansion coefficients on the details of the intramolecular potential. The first three terms of the expansion are enough to capture the essential features of the $p(c)$ that have already been calculated for symmetric odd and/or even dimers at various degrees of resolution concerning the generation of the dominant molecular conformations of the spacer.[1-4] The dominance of the $P_1 - P_3$ terms on the behaviour of the orientational coupling of the bonded mesogens is an intrinsic property of these dimers and not the circumstantial outcome of a particular modelling.

Using as the only inputs the statistics of the conformation of the dimer and the experimental values of T_{NI}, the Maier-Saupe mean field theory described in the manuscript provides the self-consistency relationships for the calculation of the full orientational/conformational distribution function of the dimer (and of its mixtures with its monomer), as well as the free energy of the systems at constant volume/composition conditions.

In our calculations for CB9CB we have chosen the set of the a_l parameters as $a_1 = 0.25 w_0$, $a_2 = 0.6 w_0$ and $a_3 = -0.35 w_0$, with $w_0/k_B \approx 1398 K$, see the main text of the manuscript for details. With this parameterisation the effective intramolecular potential $E(c)$ is presented in Figure SI3.
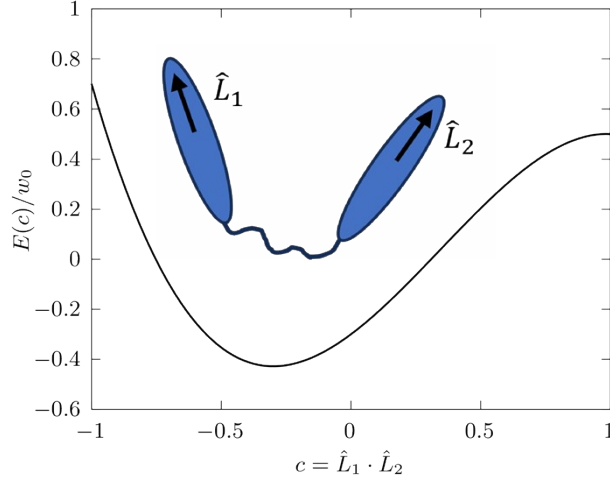
Figure SI3. Internal energy of the dimer as a function of the relative orientation of the cores. A cartoon of the dimer is presented indicating the orientation of the molecular dipoles in the mesogenic cores.

The statistics of conformations of the flexible dimers change in the nematic phase according to Eq 10 of the manuscript, due to the orientational coupling between the mesogenic units and the nematic director field. The integral of the orientational/conformational dependent probability $f^{(dimer)}(\omega, c)$ over the molecular orientations with respect to the nematic director gives the probability distribution of the angles between the mesogenic units in the bulk, $p^{(dimer)}_{bulk}(c)$.
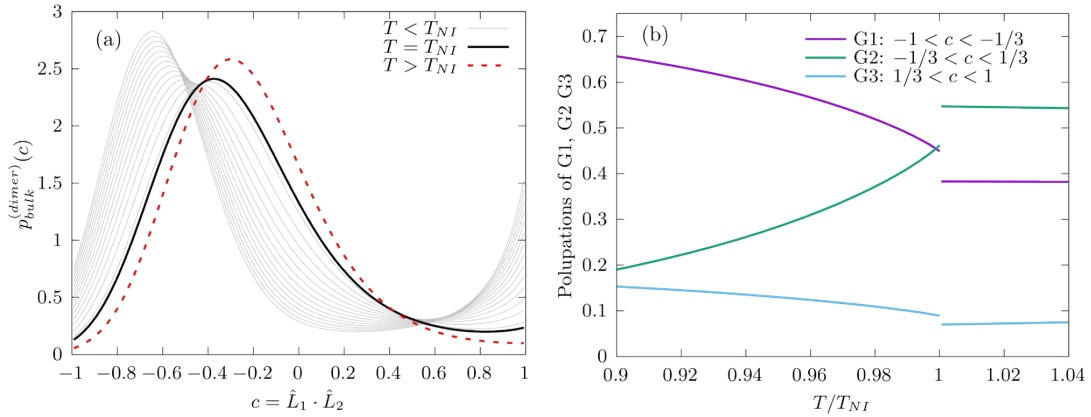

Figure SI4. (a) Probability distribution $p^{(dimer)}_{bulk}(c)$ of the model CB9CB dimer in the bulk, calculated at several temperatures. The dashed red line corresponds to a temperature slightly above T_{NI}. The thick black line gives the distribution at the onset of the nematic state, while the thin grey lines are the corresponding distributions calculated lowering the temperature at steps of $5K$. (b) Calculated populations of three sets of molecular conformations corresponding to G1 group with $-1 < \hat{L}_1 \cdot \hat{L}_2 < -1/3$ (magenta), G2 group with $-1/3 < \hat{L}_1 \cdot \hat{L}_2 < 1/3$ (green) and G3 group with $1/3 < \hat{L}_1 \cdot \hat{L}_2 < 1$ (ligh blue).

According to Figure SI4(a), $p^{(dimer)}_{bulk}(c)$ exhibits pronounced changes at the N-I transition, which are associated with the onset of long range orientational order. Comparing the distribution in the isotropic phase (red dashed curve) with the corresponding distribution at the onset of the nematic phase (thick black curve), it becomes immediately evident that the maximum

probability changes towards molecular states with larger opening angle between the mesogenic units. A noticeable increase of the U-shaped conformations is also observed. These trends continue in the nematic phase as the temperature decreases (thin grey lines). These are exactly the same trends observed in other works as well, see for instance Fig. 3 in ref. 1, where the corresponding probability distribution is referred to a dimer with 11 carbons in the spacer.

To quantify the populations of the molecular conformers corresponding to extended, folded and intermediate states, we have classified them into three different groups with respect to their opening angle $\hat{L}_1 \cdot \hat{L}_2$. The first group (G1) collects conformations with opening angle larger than ~110° ($-1 < \hat{L}_1 \cdot \hat{L}_2 < 1/3$), the third group (G3) collects the relatively folded conformations with opening angle less that ~70° ($1/3 < \hat{L}_1 \cdot \hat{L}_2 < 1$) and the rest of conformations, those with $-1/3 < \hat{L}_1 \cdot \hat{L}_2 < 1/3$, are collected in the second group (G2). In Fig. SI4(b), we present the temperature evolution of the populations of G1, G2, G3 groups. In the isotropic phase G2 is the dominant group. However, with the onset of the nematic phase G1 group of conformers becomes the dominant one and the conformers belonging to G2 group populate mainly the G1 group and to a lesser extend the G3. Deeply in the nematic phase almost 80% of the conformers belong to the G1 group and the rest to G3.

We expect, however, that the calculated increase of the population of the U-shaped conformations in the nematic phase as the temperature drops or equivalently as the orientational order parameter increases, is slightly overestimated. This overestimation is an intrinsic feature of any model that considers particles with extensive flexibility in a nematic field and assumes that the orientational coupling of each molecular conformer depends solely on the relative orientation of specific molecular segments with the nematic director. While this assumption is adequate for rigid, or almost rigid particles, it has some limitations for flexible molecules. In the case of dimers, for instance, a hairpin and a fully extended conformer experience the same ordering potential, assuming that the orientational potential of the molecular conformers of the dimer is determined solely by the orientations of its mesogenic cores with respect to the director. Excluded volume arguments, however, suggest that the strength of the ordering of the higher anisometric linear conformations in a nematic environment should be higher in comparison to the ordering strength of the less shape-anisometric U-shaped conformers. Given that in the case of odd dimers neither the linear nor the U-shaped conformations are accessible with significant probabilities in the isolated

molecule (see Figure SI4), the adopted potential of mean torque describes correctly, at least on qualitative grounds, the ordering of the dimers in the nematic field.

In the graphs of Fig. 4 in the manuscript and in the calculations that will follow in SI, we consider only the high temperature nematic phase which, according to experiment, is stable up to $T \approx 0.95T_{NI}$ for the neat CB9CB system. Bellow this temperature the nano-modulated nematic, N_x, becomes stable. See the main text of the manuscript on how the experimentally calculated temperature dependence of birefringence can be utilised to allow the calculation of the relevant order parameters and orientational correlations in the low temperature nematic phase.

The net molecular dipole moment due to the permanent dipoles, m, of a given molecular conformation having the cyanobiphenyl units pointing in the $\hat{l}_1$ and $\hat{l}_2$ directions, is given by $m = \mu_{CN}(\hat{l}_1 + \hat{l}_2)$ with, μ_{CN}, the electric dipole moment of the CN terminal group. The components of the mean-square molecular dipole along and perpendicular to the nematic director are given by: $m_{\parallel}^2 \equiv \langle (m \cdot \hat{n})^2 \rangle$ and $2m_{\perp}^2 = \langle m^2 \rangle - m_{\parallel}^2$, with $\langle m^2 \rangle = 2\big(1 + \langle \hat{l}_1 \cdot \hat{l}_2 \rangle\big)$.

We have $\langle (m \cdot \hat{n})^2 \rangle = \mu_{CN}^2\big(\langle (\hat{l}_1 \cdot \hat{n})^2 + (\hat{l}_2 \cdot \hat{n})^2 \rangle + 2\langle (\hat{l}_1 \cdot \hat{n})(\hat{l}_2 \cdot \hat{n}) \rangle\big)$, which can be rewritten as

$$\langle (m \cdot \hat{n})^2 \rangle = \mu_{CN}^2 \langle (\hat{l}_1 \cdot \hat{n})^2 + (\hat{l}_2 \cdot \hat{n})^2 \rangle \left(1 + 2\frac{\langle (\hat{l}_1 \cdot \hat{n})(\hat{l}_2 \cdot \hat{n}) \rangle}{\langle (\hat{l}_1 \cdot \hat{n})^2 + (\hat{l}_2 \cdot \hat{n})^2 \rangle}\right).$$ Inserting into the last equation the definition of the nematic orientational order parameter associated with the ordering of the CB units of the dimer, $S_d = \langle P_2(\hat{l}_1 \cdot \hat{n}) + P_2(\hat{l}_2 \cdot \hat{n}) \rangle/2$, we obtain the mean-square of the total molecular dipole along the nematic director, $m_{\parallel}^2 = 2\mu_{CN}^2\frac{1}{3}(1 + 2S_d)g_{1,\parallel}^{(intra)}$,

$g_{1,\parallel}^{(intra)} = 1 + 3\dfrac{\langle (\hat{l}_1 \cdot \hat{n})(\hat{l}_2 \cdot \hat{n}) \rangle}{1 + 2S_d}$, which are the first two equations in Eq. (7) of the manuscript.

In Figure SI5 we present the temperature dependence of the various *intra*molecular correlations, which are involved in the calculation of the intramolecular g-factors: $\langle \hat{l}_1 \cdot \hat{l}_2 \rangle_b$, $\langle (\hat{l}_1 \cdot \hat{n})(\hat{l}_2 \cdot \hat{n}) \rangle_b$ and $\langle (\hat{l}_1 \cdot \hat{n}_\perp)(\hat{l}_2 \cdot \hat{n}_\perp) \rangle_b$ with $\hat{n}_\perp$ a direction perpendicular to the nematic director. We note here that the close to zero values of $\langle (\hat{l}_1 \cdot \hat{n}_\perp)(\hat{l}_2 \cdot \hat{n}_\perp) \rangle_b$ should not interpreted as a result of the lack of orientational correlations between the mesogenic cores, but rather as a specific property related to the form of the probability distribution, $p_{bulk}^{(dimer)}(c)$, of the relative orientations of the mesogenic cores in the bulk. With the adopted parameterisation, we get for a single CB9CB dimer in an isotropic environment at $T = 400K$,

$\langle \hat{L}_1 \cdot \hat{L}_2 \rangle_b \approx -0.2$ indicating a weak antiparallel intramolecular dipolar correlation, note that in the graph we present the temperature dependence of $\langle \hat{L}_1 \cdot \hat{L}_2 \rangle_b / 3$. In the nematic phase and as the temperature drops the antiparallel correlation is strongly enhanced as result of the orientational coupling of the mesogenic units with the nematic field. This is clearly demonstrated by the jump of $\langle (\hat{L}_1 \cdot \hat{n})(\hat{L}_2 \cdot \hat{n}) \rangle_b$ at the NI phase transition and its temperature dependence in the nematic phase (magenta curve in Fig. SI5). Given the positive contribution of the U-shaped conformation (G3-group) to $\langle (\hat{L}_1 \cdot \hat{n})(\hat{L}_2 \cdot \hat{n}) \rangle_b$, the significantly below zero obtained values of this correlation in the nematic phase develop mainly from the enhancement of the elongated conformations(G1-group).
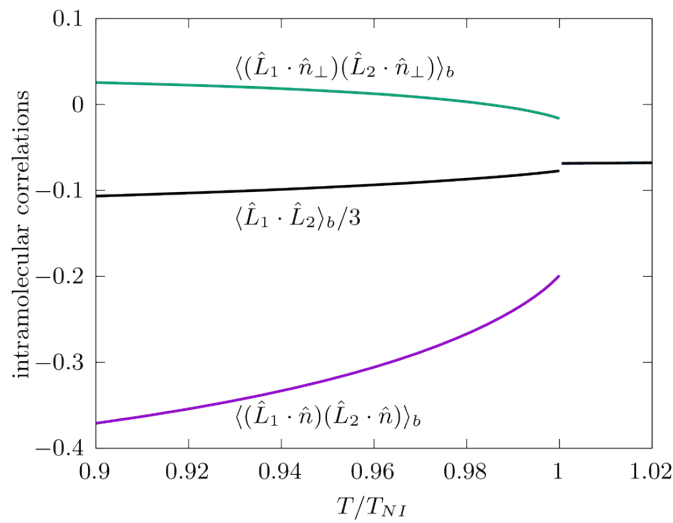

Figure SI5. *Intramolecular orientational correlation factors vs reduced temperature for the neat CB9CB system.*

In Figure SI6 we present the temperature dependence of (a) the orientational order parameter S_d of the dimer which, by definition, is the order parameter associated with the ordering of the CB groups of the molecule, and (b) the mean square components of the scaled dipole moment, m_λ^2/μ_{CN}^2. From Figure SI6(b) it is evident, that while $m_\perp^2$ decreases with decreasing temperature in the nematic phase, the parallel component $m_\parallel^2$, remains relative insensitive to temperature variations. In the isotropic phase m^2 remains practically constant. While the temperature dependence of $m_\perp^2$ is in qualitative agreement with the behaviour of $\varepsilon_\perp$ (dielectric constant perpendicular to the nematic director), the temperature dependence of $m_\parallel^2$ is in remarkable disagreement with the experimentally measured $\varepsilon_\parallel(T)$, which after a small jump at the NI phase transition drops rapidly upon lowering the temperature. In addition, the practically constant mean-square dipole moment in the isotropic phase is also in disagreement with the relative strong variation of the measured dielectric constant with

temperature in the isotropic phase, see Fig. 4(a) in the manuscript. These observations, suggest that for a quantitative reproduction of the dielectric permittivity in terms of the Kirkwood-Fröhlich theory, the ignored, up to this point, *inter*molecular dipole-dipole correlations, i.e. considering that $g_{1,\parallel(\perp)}^{(inter)} = 1$ in Eq. (5) of the manuscript, should be taken into consideration for the calculation of the components $[\mu^2]_{\parallel(\perp)} = m_{\parallel(\perp)}^2 g_{1,\parallel(\perp)}^{(inter)}$ of the effective mean square dipole moment. Actually, this is one of the main topics discussed in the manuscript.
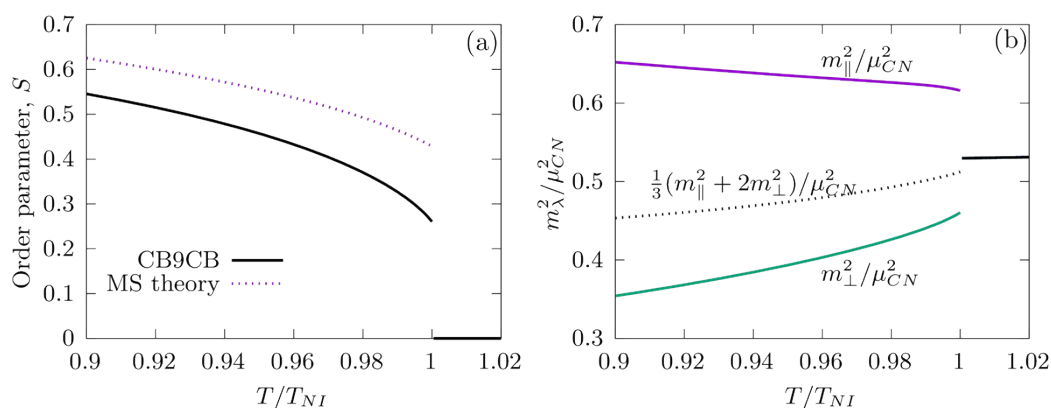

Figure SI6. *(a) Orientational order parameter of the neat CB9CB dimer system vs reduced temperature (solid line). For comparison in the same plot the universal Maier-Saupe nematic order parameter for rigid rod-like mesogens is also presented (dotted line). (b) Mean square components of the scaled dipole moment vs reduced temperature (solid lines); the dotted line is the average mean square dipole moment.*

References

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