Hierarchical propagation of chirality through reversible polymerization: the cholesteric phase of DNA oligomers

Cristiano De Michele[1,*], *Giuliano Zanchetta*[2], *Tommaso Bellini*[2], *Elisa Frezza*[3] *and Alberta Ferrarini*[3]

[1]*Dipartimento di Fisica, "Sapienza" Università di Roma, Piazzale A. Moro 2, I-00185 Roma, Italy.*
[2] *Dipartimento di Biotecnologie Mediche e Medicina Traslazionale, Università di Milano, v. F.lli Cervi 93, Segrate (MI) Italy.*
[3] *Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1, I-35131 Padova, Italy.*

[*]cristiano.demichele@roma1.infn.it

Although chiral nematic ordering has been repeatedly observed and studied in various lyotropic systems [1], a quantitative account for the macroscopic chirality on the basis of the chiral structure of its microscopic constituents represents a challenge for theory and computations. Here, we consider the chirality of the nematic ordering that develops in solutions of palindromic DNA dodecamers via their self-assembling into weakly bound linear chains. In this system the cholesteric pitch has a non-trivial dependence on both DNA concentration and temperature. In order to grasp a physical understanding of this complex behavior, we developed a novel theoretical approach that bridges the structure and chirality of the elementary building blocks to the helical organization of the self-assembly-driven cholesteric phases. Our theoretical approach combines an Onsager-like theory for orientational order, extended to the elastic and chiral properties of the cholesteric phase, with a theory for self-assembly-driven nematic liquid crystals [2]. Noticeably, our theory contains no adjustable parameters other than those previously determined from the phase behavior. We also performed new accurate experimental measurements of the cholesteric pitch, as a function of temperature in samples at different concentrations. In these samples a right-handed cholesteric phase is formed, with a pitch of few microns, which increases with lowering temperature and increasing concentration. The good quantitative agreement (see Figure) between theoretical and experimental results allows us to unveil the physical mechanisms at play in the propagation of chirality and to identify in the temperature and concentration dependence of the pitch an hallmark of self-assembly.

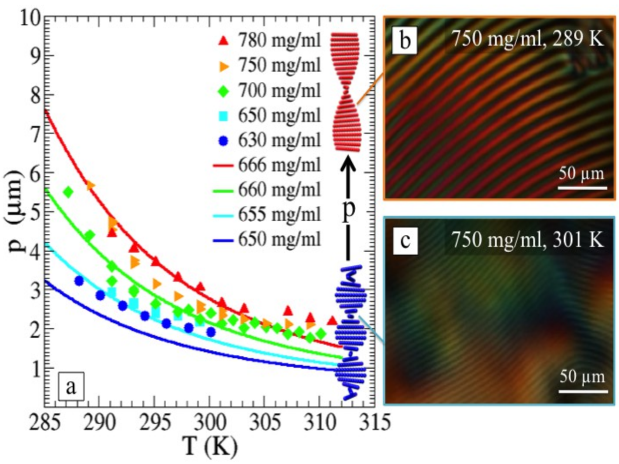

Figure Comparison of experimental and theoretical pitch for liquid crystal cholesteric solutions of Dickerson dodecamer. (a) Pitch as a function of temperature along isochores, from experiment (symbols) and theory (lines). Concentrations (mg/ml) are given in the legend. (b) and (c) show cholesteric textures for two different state points.

References

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