

Simultaneous Chirality Transfer and Structured Aggregation of a Cyclopeptide in a Liquid Crystal

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1. Thermal Phase Transitions

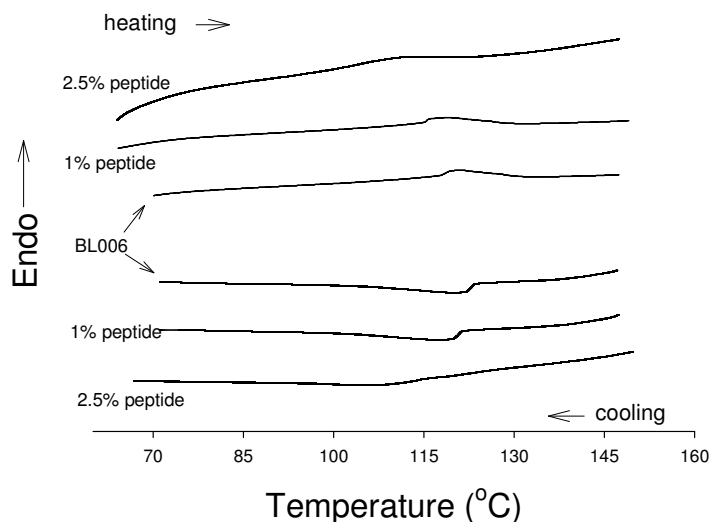


Figure S1 DSC heating and cooling curves of pure nematic liquid crystal BL006 and its mixtures with 1% and 2.5% of peptide. As a result of the reduced propensity for intermolecular stacking, the cyclopeptide has a good solubility in the used nematic LC, BL006 (Merck). This can be noticed from the DSC heating and cooling curves in Figure S1. On heating, pure BL006 shows an endothermic peak (nematic-to-isotropic phase transition) at about 119 °C, while the clearing temperature decreases upon addition of the cyclopeptide in the LC host, to ~ 117 °C with 1 wt% of the peptide dopant and 112 °C with 2.5%. Similar effect on the isotropic-to-nematic phase transition temperature upon cooling is visible. This result indicates that at these concentrations cyclopeptide molecules are basically solubilized in the LC host and behave like miscible non-LC component resulting in a reduction of the LC phase transition temperatures.

2. Effect of Cooling Rate and Cyclopeptide Concentration

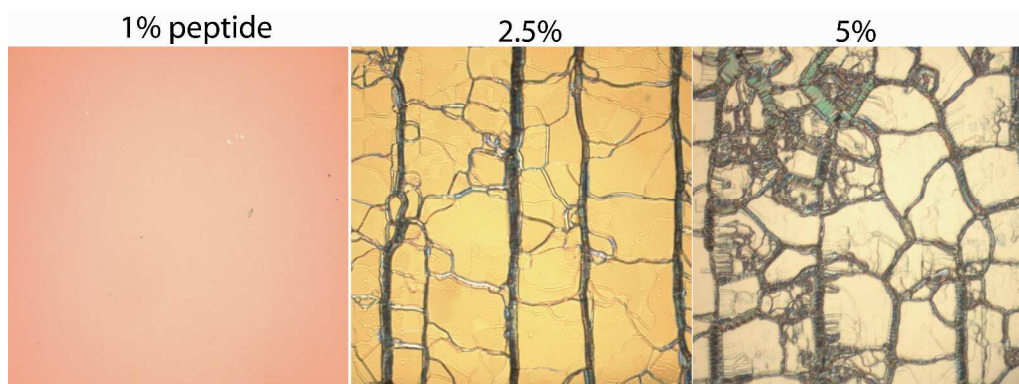


Figure S2 Polarizing optical microscope images at room temperature for BL006 doped with 1%, 2.5% and 5% of peptide, respectively. The mixtures were placed in a parallelly-rubbed liquid crystal cell (10 μm gap) and slowly cooled from 130 $^{\circ}\text{C}$ (isotropic phase) to room temperature at a cooling rate of 0.2 $^{\circ}\text{C}/\text{min}$ (image size: 425 μm \times 425 μm). These POM images were recorded at room temperature for BL006 doped with 1%, 2.5% and 5% of peptide and, instead of quenching, cooled very slowly (~ 0.2 $^{\circ}\text{C}/\text{min}$) from the isotropic state (130 $^{\circ}\text{C}$). The planar texture of BL006 with 1% of cyclopeptide is defect-free because of the long annealing time available for cholesteric LC to eliminate the defects. With 2.5% of peptide, despite the slow cooling, aggregation of a fraction of cyclopeptide molecules takes place and results in aggregates that interconnect and stabilize the “oily streak” defects. Many (not all) of the peptide aggregates develop a preferential alignment along the surface rubbing direction as shown in the figure. When the peptide concentration is further increased to 5%, an increased number of aggregates and defects are developed, forming a denser network in the planar texture.

3. POM Observation of Mixtures under the Effect of an Electric Field

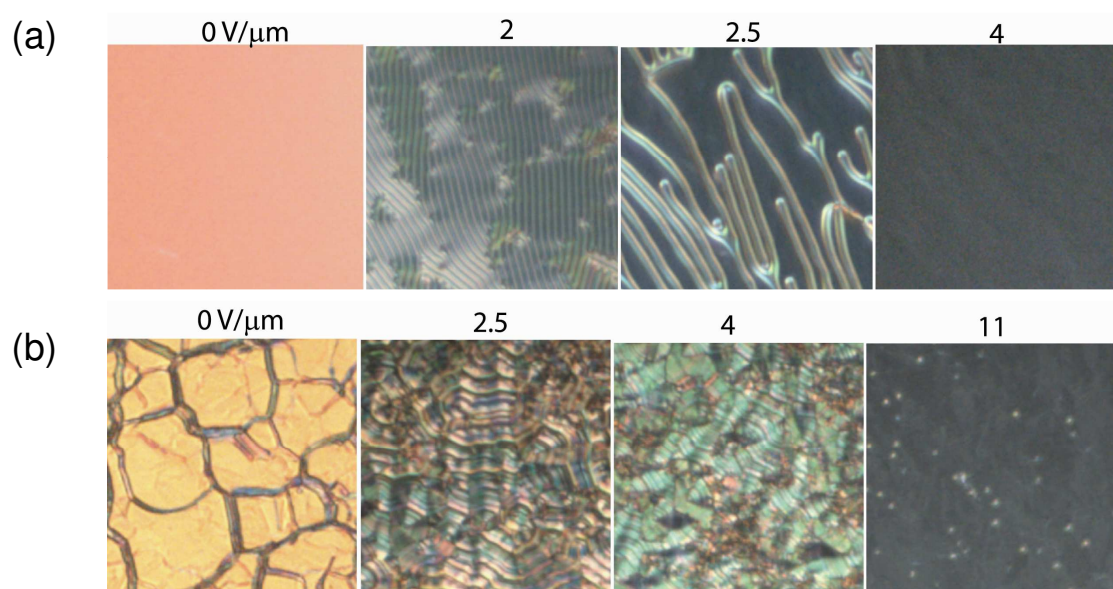


Figure S3. POM images (84 μm \times 84 μm) recorded for BL006 containing (a) 1% and (b) 2.5% of peptide at indicated voltages. The network of defects affects the transition from the planar to the homeotropic texture.

4. Comparison with a Commercially Available Chiral Dopant

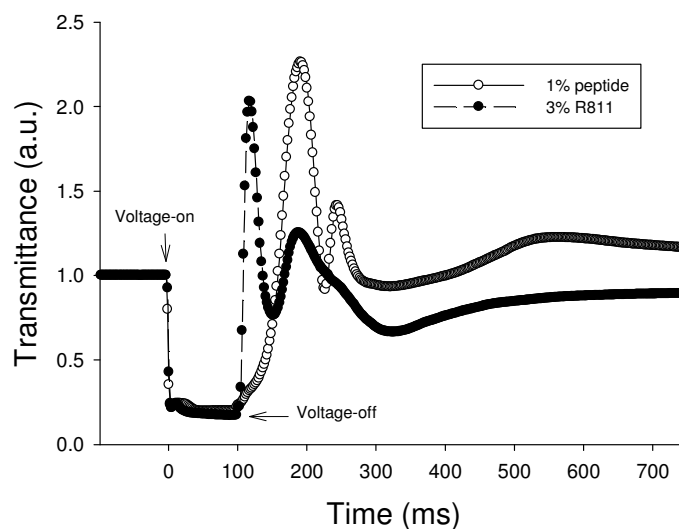
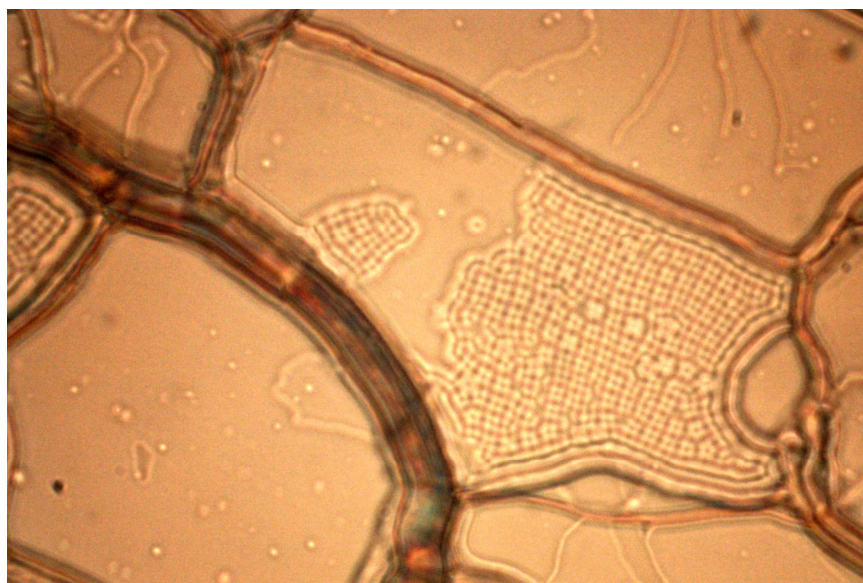


Figure S4 Transmittance change in response to one square-wave electric pulse of 100 ms (5 V/ μ m at voltage-on and 0 V at voltage-off) for BL006 doped with, respectively, 1% of peptide and 3% of R811 (a chiral dopant from Merck). The mixtures were placed in a parallelly-rubbed liquid crystal cell (10 μ m gap) and slowly cooled from 130 $^{\circ}$ C (isotropic phase) to room temperature at a cooling rate of 0.2 $^{\circ}$ C/min. Both mixtures display the same fast switching-on time, while the switching-off time and the time of dynamic instability at the field-off state are slightly longer for BL006 doped with the cyclopeptide.

5. Cyclopeptide-Induced Square-Lattice Pattern



36 μ m

Figure S5 Polarizing optical microscope image showing regions with a square-lattice pattern, obtained with BL006 doped with 5% of peptide, slowly cooled from 130 °C to room temperature (cooling rate: 0.2 °C/min) in a parallelly-rubbed liquid crystal cell (10 µm gap). The aggregates of the cyclopeptide interact with the cholesteric LC host and may distort the LC director configuration. The POM image reveals the formation of a two-dimensional square-lattice pattern in some areas surrounded by the aggregates. Such a texture, formed by superposition of orthogonal one-dimensional undulations, is known for cholesteric LC with initially a planar texture and subjected to a weak electric field under certain conditions (frequency, voltage and the ratio of cell thickness to helical pitch). [1,2] The fact that it is observed in the cyclopeptide-doped BL006 in the absence of an electric field is intriguing. This observation suggests that the peptide aggregate-LC interfacial interaction could align LC molecules perpendicularly to the substrate plane, similar to the distortion created by a weak electric field on the planar texture required for such two-dimensional undulations. The exact conditions leading to the formation of a square-lattice pattern without the action of an electric field are unknown, and the non-homogeneity of the peptide aggregates (thickness, for example) may explain why the lattice is not formed everywhere.

References

- (1) Senyuk, B. I.; Smalyukh, I. I.; Lavrentovich, O. D. *Opt. Lett.* **2005**, *30*, 349-351.
- (2) Kang, S.-W.; Chien, L.-C. *Appl. Phys. Lett.* **2007**, *90*, 221110.