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

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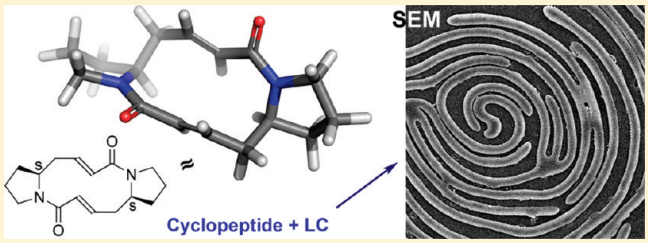
Supporting Information

ABSTRACT: We report the finding that a chiral cyclopeptide dissolved in a nematic liquid crystal (LC) host could aggregate in a manner that is controlled by the texture (LC director configuration) of a cholesteric phase that is induced by the cyclopeptide itself. On one hand, with the fingerprint texture, where the helical axis formed by rotating LC molecules, that lies in the substrate plane, the cyclopeptide can use the LC texture as a template to aggregate and form long-range-ordered ribbons that mimic the helical configuration of the LC director. On the other hand, with the planar texture, where the helical axis is normal to the substrate plane, the cyclopeptide can migrate into the "oily-streak" defect regions of the cholesteric phase and stabilize a network of defects that dictates the electrooptical response of the LC. This is the first example of a molecular species exhibiting such a structured aggregation and defect stabilization effect in a cholesteric LC, but similar phenomena were previously reported for platinum nanoparticles and silica colloidal particles, respectively, dispersed in a cholesteric LC host. This study provides more evidence for the potential interest of exploring LCs as an anisotropic medium for mediating the aggregation and assembly of cyclopeptides.



INTRODUCTION

There has been a growing interest in mixing a liquid crystal (LC) host with another component that may be composed of molecules, nanoparticles, or colloidal particles.[1−7] Generally, the benefit is one of the following: the electrooptical response of the LC is improved, the LC is endowed with a new function, or the added species can be organized via the LC medium acting as an ordered template. To name a few examples, a self-assembled LC gel was shown to exhibit faster electrooptical switching than the LC host;[1] nematic LCs with positive dielectric anisotropy doped with gold nanoparticles (AuNP's) could have a dual alignment mode and electrooptical response with a reduced threshold voltage;[2] dissolving an azo dye in ferroelectric LCs made it possible to switch the polarization optically;[3] quantum dots (QD) dispersed in LCs could have their photoluminescence intensity switched electrically;[4] carbon nanotubes could be aligned by LCs;[5] and nanoparticles could be patterned in a cholesteric LC template.[6] Clearly, there are numerous possibilities to explore such LC-based mixtures, and the perspective of making new discoveries is exciting.

In a previous paper,[7] we reported the finding that a cyclopeptide dissolved in a nematic LC could self-assemble upon cooling from an initially homogeneous mixture, resulting in millimeter-long hollow tubes with micrometer-sized diameters in contrast to compact crystals formed by the same cyclopeptide in organic solvents. The finding illustrates the important role played by the interaction of cyclopeptide with ordered LC molecules in the assembly process. Similar to what is known with self-assembled LC gels[8] for which dissolved gelator molecules could aggregate into nanofibers, the assembly of cyclopeptide molecules in an LC host is strongly influenced by the competition between the propensity for cyclopeptide molecules to stack on each other, forming nanotubes, and their solubilization by the LC solvent. To investigate further the use of LCs to mediate the assembly of cyclopeptides, in the present study we designed and synthesized a novel cyclopeptide that bears two chiral centers and has no secondary amides for intermolecular hydrogen bonds. We envisioned that these new features should reduce the propensity for intermolecular stacking of cyclopeptide molecules and favor their interactions with the LC host. We report herein that these structural changes indeed result in completely different but equally fascinating behaviors of the cyclopeptide in a nematic LC. Whereas at low concentrations (∼1 wt % with respect to the LC host) the cyclopeptide simply acts as a chiral dopant to convert the nematic LC into a cholesteric LC, at higher concentrations (>2%) it can simultaneously induce the cholesteric phase and self-assemble into aggregates in a manner controlled by the surrounding cholesteric LC texture. With the fingerprint texture, the cyclopeptide can use the LC as a template and aggregate into long-range-ordered ribbons that mimic the helical configuration of the LC director in the cholesteric phase induced by the peptide itself. With the planar texture, cyclopeptide molecules can migrate into the "oily-streak" defect regions and stabilize a network of

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defects, which determines the electrooptical behavior of the cholesteric LC.

EXPERIMENTAL SECTION

The nematic LC used, BL006, was purchased from Merck. To prepare a mixture of BL006/cyclopeptide with a given concentration of peptide, the two constituents were dissolved in a small amount of chloroform (about 0.5 mL for 100 mg of the LC) to ensure the homogeneity of the mixture. Afterwards, two preparation procedures were employed. In one case, after part of the solvent was evaporated in a vacuum oven at room temperature, the BL006/cyclopeptide mixture was cast on a glass slide to form a thin film before being further annealed at 60 °C for 2 h to remove the solvent. Samples prepared in this way were used to obtain the fingerprint texture. In the other case, the mixture was dried completely in a vacuum at 60 °C before being flow filled and warmed to 70 °C in a parallel-rubbed indium tin oxide (ITO)-coated electrooptical cell with a gap of 10 μm (EHC Japan). These samples were used to obtain the planar texture and for the electrooptical measurements. Unless otherwise stated, prior to measurement, the mixture was held at 130 °C (isotropic phase) for 10 min and then cooled to room temperature. The electrooptical response was measured by using a setup detailed previously.[9] In essence, an electrooptical cell was placed between two crossed polarizers on a polarizing optical microscope (POM, Leitz DMR-P); by replacing the digital camera used to take photomicrographs with a high-speed photodetector (Melles Griot) connected to a digital oscilloscope (Tektronix, TDS 420A), the change in transmittance of the cell under a voltage could be measured. A high-voltage waveform generator (WFG-500, FLC Electronics) was used to apply either a sinusoid wave ac field (1000 Hz) or a pulse electric field across the cell. The POM equipped with an Instec hot stage was also used to observe the cholesteric LC textures. After the extraction of BL006 in hexane, the cyclopeptide aggregates were examined by using a tapping-mode atomic force microscope (AFM, Nanoscope IV) and an emission gun scanning electron microscope (SEM, Hitachi S-4700). In addition, a differential scanning calorimeter (DSC, TA-Q200) was used to measure the LC phase transitions in cyclopeptide-doped BL006 at a heating or cooling rate of 10 °C min^{-1} (Supporting Information).

RESULTS AND DISCUSSION

The synthesis and structure of novel cyclopeptide **1** are depicted in Figure 1. The same cyclooligomerization method that was used to prepare **2** from its linear precursor **6** was applied to the synthesis of **1** from **5**.[10] The latter was easily prepared in a few steps from Boc-Pro, first involving the preparation of diazoketone **3**, followed by a Wolff rearrangement to yield ester **4**.[11] This ester was then transformed into pentafluorophenyl ester **5** following well-established procedures in our laboratories.[9] Similar to cyclopeptide **2** used in our previous work,[7] **1** is also a 12-membered lactam with C_2 symmetry and an *E*-alkene moiety imparting rigidity as well as solubility. However, unlike **2**, it bears two chiral centers of identical S configuration that completely dictates the shape of the molecule as a rigid rectangle, and it has no secondary amides required for intermolecular hydrogen bonds that favor cyclopeptide molecule stacking to form nanotubes.[7] Nonetheless, **1** can crystallize from solution (organic solvents) through dipole−dipole and van der Waals interactions.[12]

BL006 (Merck), a nematic LC having a clearing temperature of ~119 °C, was used as the host. Cyclopeptide **1** was first dissolved in BL006 at 130 °C and then cooled to room temperature unless otherwise stated. The long-range-structured aggregation of the cyclopeptide is shown in Figure 2. The polarizing optical microscope (POM) image in part a was recorded from a thin film

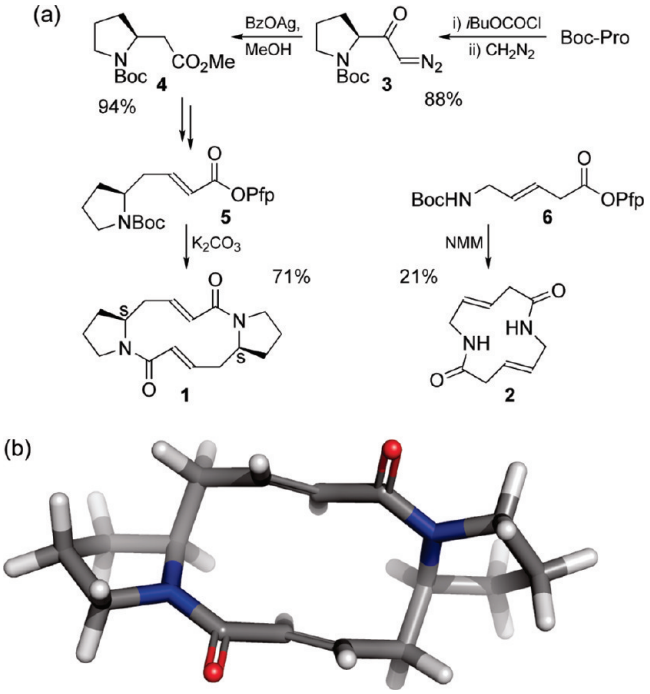

Figure 1. (a) Comparative syntheses of cyclopeptides **1** and **2**. (b) Three-dimensional stick model of **1**.

(~10 μm) of the BL006/cyclopeptide (2.5%) mixture cast on a glass plate. The fingerprint texture (periodic lines) is characteristic of a cholesteric phase (i.e., chiral nematic phase with a helical configuration LC director). Because BL006 is nematic, this clearly indicates that solubilized cyclopeptide molecules act as a chiral dopant of the LC host and induces the cholesteric phase. It is seen that the undulation lines of the fingerprint texture, where the helical axis of the rotating LC director lies in the substrate plane, are deformed by constraints related to defect domains. Dark lines are regions where LC molecules are oriented perpendicularly to the substrate surface, and the distance between two dark lines in image a is about 2 μm, that is, the half-pitch of the helix. The SEM image in b was obtained from the same sample after the extraction of BL006 from the mixture. This was achieved by dipping the mixture on the glass plate in hexane for 2 h to remove the nematic host,[13] followed by drying in air. Aggregates of cyclopeptide were found on the substrate surface that, surprisingly, form periodic ribbons mimicking the fingerprint texture of the cholesteric phase. The pattern of the cyclopeptide aggregates "copies" the long-range molecular ordering as well as the topological constraints in the cholesteric LC phase. This can be noticed from the many circular and U-turned ribbons (image b) that reflect the organization of defects of the LC texture (image a). The ribbons are uniform in width, and the average distance between them is about 0.8 μm, which is smaller than the half-helical pitch of the cholesteric phase. The AFM height image in c shows a region of aligned ribbons, and the height profile indicates a thickness of about 200 nm for the cyclopeptide aggregates. We note that in regions where the POM image shows no clear fingerprint texture but domains apparently contain more cyclopeptide aggregates, after the extraction of BL006 a porous network of peptide sheets could be observed.

This striking phenomenon is reminiscent of the assembly of platinum nanoparticles (NPs) dispersed in a cholesteric LC.[6] In that study, without removing the LC, TEM investigations found

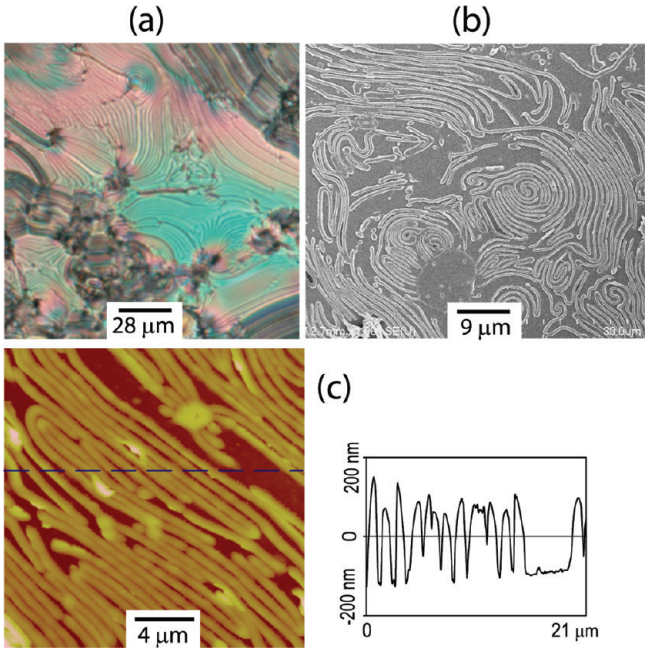

Figure 2. (a) Polarizing optical microscope (POM) image of a mixture of BL006/peptide (2.5%) cast on a glass plate, (b) scanning electron microscope (SEM) image of the mixture after the extraction of BL006 in hexane; and (c) atomic force microscope (AFM) height image of the mixture after the extraction of BL006, where the height profile corresponds to the marked scanning line.

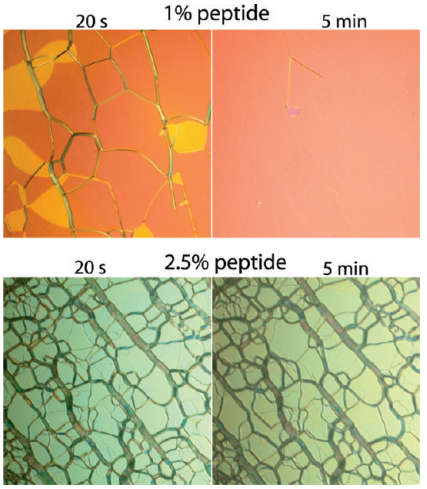

Figure 3. Polarizing optical microscope images of BL006 containing 1 and 2.5% peptide, respectively. The mixtures were placed in a parallel-rubbed LC cell (10 μm gap) and quenched from 130 °C (isotropic phase) to 108 °C (cholesteric phase). The quenching took about 20 s, and the images were recorded immediately after and 5 min later. Image size: 298 μm × 298 μm.

that NPs were disposed of in regions where LC molecules are parallel to the film plane instead of where they are perpendicular, giving rise to ribbons formed by nonaggregated NPs that mimic the fingerprint texture. However, the distance between the ribbons of NPs is much larger than the helical pitch of the cholesteric phase (about twice the pitch), in contrast to the present case with aggregated cyclopeptide for which the period of the ordered ribbons is smaller than the helical pitch of the cholesteric phase. It was suggested that the organization of platinum NPs could occur during annealing of the mixture with NPs migrating into regions containing more free volume. In a follow-up report,[14] the same authors showed evidence that NPs were essentially located at the LC−air interface. Now, on the basis of this reported case of NPs, the following analysis can be made for our cyclopeptide-doped LC. The mixture of BL006 and the peptide cast on the glass slide contained some solvent (chloroform), and it was annealed at 60 °C to remove the solvent. During solvent evaporation, a fraction of cyclopeptide molecules are miscible with BL006 and induce the cholesteric phase, while simultaneously another fraction of cyclopeptide molecules aggregate in regions with a certain LC molecular orientation. It is possible that the aggregation occurs at an interface because, understandably, the interfacial tension may depend on the orientation of LC molecules (parallel or perpendicular). The fact that the ribbons of peptide aggregates are stable after the LC host is removed in hexane suggests that the aggregation could occur at the interface with the substrate because if they were at the LC−air interface, as in the case of platinum NPs,[6,14] the patterned aggregates or assembly could not be retained while removing the LC solvent. The process of LC extraction may also affect the final organization and aggregation state of the cyclopeptide. However, chloroform should have little effect on the observed aggregation behavior. This common solvent was used to ensure a homogeneous mixture of BL006/cyclopeptide; the induction of the cholesteric phase and the long-range-ordered aggregation mimicking the fingerprint texture, upon removal of the solvent, reflect a balance between the intermolecular interactions of the cyclopeptide and LC molecules and the intermolecular interactions within the two constituents. Though a clear understanding of the structured aggregation requires more investigation, what is clear is that in both cases the spatial segregation of either platinum NPs or cyclopeptide molecules inside the cholesteric LC host, followed by aggregation in the latter case, is related to the orientation of LC molecules that rotate in the substrate plane as determined by the helical configuration of the LC director. A remarkable feature of the cyclopeptide is that it induces the chiral LC phase by itself and simultaneously uses it as a template for its long-range-ordered aggregation.

As mentioned above, with the fingerprint texture, the helical axis formed by rotating LC molecules lies in the substrate plane, which creates interfacial regions having different LC molecular orientations. This situation no longer exists with the planar texture formed by cholesteric LCs in a parallel-rubbed electro-optical cell in which LC molecules are uniformly oriented along the rubbing direction at the interface with the substrate and the helical axis is perpendicular to the substrate plane.

We thus conducted experiments by placing the BL006/cyclopeptide mixture in a parallel-rubbed ITO-coated cell with a 10 μm gap to determine how the cyclopeptide could assemble in such a different LC environment. We found that instead of forming long-range-ordered ribbons, cyclopeptide molecules could migrate into the oily-streak defect regions and stabilize them, similar to a finding made with silica colloidal particles dispersed in a cholesteric LC.[15] Figure 3 shows POM images of BL006 containing 1 and 2.5% cyclopeptide, respectively, taken at 108 °C immediately after quenching from the isotropic state (130 °C) (the cooling took about 20 s) and 5 min later. In the case of BL006 with 1% cyclopeptide, upon the formation of a cholesteric phase, a planar texture is formed with oily-streak defects. Because these defects composed of disclinations are unstable,

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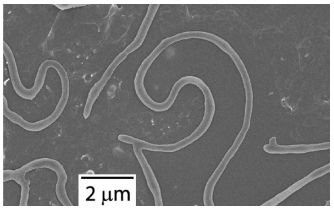

Figure 4. Scanning electron microscope (SEM) image of the BL006/peptide (2.5%) mixture adopting the planar texture, after the extraction of BL006 in hexane.

they disappear almost completely 5 min later as a result of a coarsening process. This observation, which is typical of a cholesteric LC under our conditions, indicates that at the low concentration of 1% all cyclopeptide molecules are solubilized in the LC host and act as a chiral dopant. By contrast, with 2.5% of the cyclopeptide in BL006 subjected to the same quenching process, there are an increased number of oily-streak defects upon cooling to 108 °C and they are stable in time and show little evolution after 5 min. Actually, the same defect network remained after 1 h at this temperature (image not shown). This result indicates that whereas part of the cyclopeptide remains solublized in BL006 and induces the cholesteric phase leading to the planar texture, the other part tends to segregate from the LC host and migrate into the high-free-energy defect regions. Similar to the situation for colloidal particles,[15] the defect-mediated aggregation of the cyclopeptide prevents the coarsening process from occurring and thus stabilizes the network of defects. For the mixture with 2.5% cyclopeptide, after dipping the electrooptical cell in hexane to remove BL006 and then carefully using a blade to separate the two glass plates, SEM observation found threads of peptide aggregates on the substrate surface with no long-range ordering (Figure 4).

As expected, the aggregation of the cyclopeptide and the stabilization of a network of defects hold consequences for the electrooptical response of the cholesteric LC. The two mixtures were slowly cooled from the isotropic state to room temperature (~0.2 °C/min), and their optical transmittance under crossed polarizers was monitored as a function of applied voltage; the results are shown in Figure 5. For BL006 containing 1% peptide, the reorientation of LC molecules along the electric field direction takes place at ~2 V/μm (threshold voltage) and the transmittance reaches the minimum level with the formation of the homeotropic texture (LC molecules oriented perpendicularly to the substrate surface). The planar-to-homeotropic texture transition is reversible, as revealed by the recovered transmittance upon decreasing voltage. For BL006 containing 2.5% peptide, the stabilization of a network of defects by aggregated cyclopeptides results in different electrooptical responses to the electric field. The transmittance starts to fall at almost the same threshold voltage as for the mixture with 1% peptide, but it cannot go on to drop to the minimum level because the planar-to-homeotropic texture transition is hampered by the network of defects. At 2.5 V/μm, the electric field could only destabilize the planar texture, resulting in the fingerprint texture. As the field strength further increases from 3 to 6 V/μm, the cholesteric LC texture evolves from the fingerprint to a focal conic texture arising from randomly aligned helical axes. Only at voltage >6 V/μm is the electric field strong enough to reorient LC molecules homeotropically and bring the transmittance to a minimum level. Upon voltage reversal, the network of defects prevents the planar

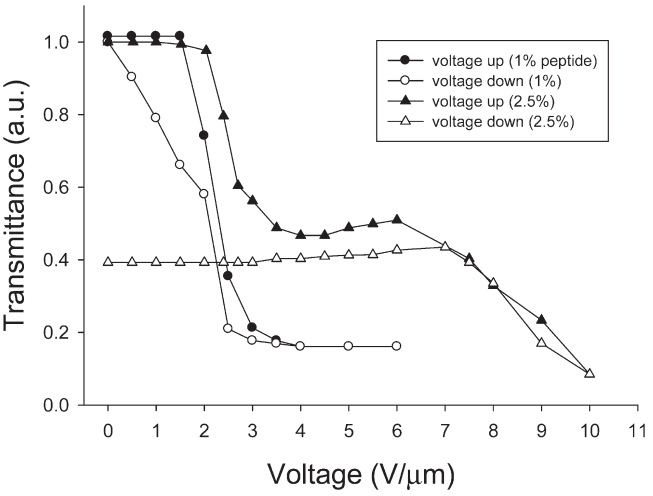

Figure 5. Normalized transmittance vs applied voltage for BL006 containing **1** and 2.5% cyclopeptide, with the mixture being placed in a parallel-rubbed liquid crystal cell (10 μm gap) and slowly cooled from 130 °C to room temperature (cooling rate 0.2 °C/min).

texture from being reformed; the transmittance is only partially recovered to the level corresponding to the focal conic texture. We note that despite the network of defects where peptide aggregates are located, no LC gel was observed with the concentrations of cyclopeptide used.

Although the cyclopeptide could crystallize from solution in an organic solvent, we found no evidence that the aggregates in the LC host are crystalline.[12] First, the aggregates remaining in the glass plate after the extraction of BL006 (Figures 2 and 4) exhibited no birefringence when viewed with the polarizing microscope. Second, for the aggregates that formed with planar texture, the apparent birefringence appears to come from the LC host. In the case of BL006 containing 2.5% peptide, as LC molecules are reoriented by the electric field, the long aggregates forming the initial network (Figure 3) disappeared, with only a number of birefringent spots remaining, which are likely from LC molecules trapped in the peptide aggregates (POM images in the Supporting Information).

The present study was designed on the basis of our previous work on cyclopeptides.[7] The results show that a structural modification of the cyclopeptide can have a drastic effect on its assembly behavior in an LC host, which is the result of a change balance between the interactions of the peptide and the LC and the interactions within the peptide. However, there is no reason to believe that the simultaneous chirality transfer and long-range-ordered aggregation in a nematic LC is unique to cyclopeptide. The question can be raised as to whether a nonpeptide chiral compound can exhibit the same assembly behavior. This will be the subject of our future studies.

■ CONCLUSIONS

We investigated the aggregation behavior of a novel cyclopeptide (**1** in Figure 1) in a nematic LC. We found that the cyclopeptide, bearing two chiral centers and containing no secondary amide groups required for intermolecular H bonds, behaves very differently than a cyclopeptide that has a strong propensity for H-bond-driven intercycle stacking (**2** in Figure 1).[7] It simultaneously exhibits the chirality transfer to the nematic LC host, inducing a cholesteric phase, and long-range structured aggregation

mediated by the cholesteric texture. At a low concentration (about 1 wt % with respect to the LC host), it is completely soluble in the LC even at room temperature and acts as a chiral dopant for the nematic LC. At higher concentrations (>2%), whereas a fraction remains soluble in the LC host and induces a cholesteric phase, the rest segregates from the LC and aggregates in a manner that is controlled by the texture of the cholesteric LC phase induced by it. With a fingerprint texture, where the helical axis formed by rotating LC molecules lies in the substrate plane, the cyclopeptide uses it as an ordering template and its aggregation mimics the helical configuration of the LC director. This results in long-range-ordered peptide ribbons that are observable after the extraction of the LC host in hexane. The period of the ribbons is smaller than the helical pitch of the cholesteric LC. With a planar texture, where the helical axis is normal to the substrate plane, segregating peptide molecules move to the oily-streak defect regions and stabilize a network of defects, which affects the electrooptical response of the LC. These phenomena were previously reported for platinum nanopaticles, whose non-aggregated assembly could mimic the helical configuration of a cholesteric LC,[6] and silica colloidal particles, whose aggregation could stabilize the oily-streak defects.[15] To our knowledge, this is the first example where a molecular species, such as the used cyclopeptide, can exhibit such structured assembly and defect stabilization in a cholesteric phase that it induces itself by acting as a chiral dopant. This study, together with our previous report,[7] provides appealing evidence for the potential interest of exploring LCs as an anisotropic medium for mediating the assembly and organization of molecules such as cyclopeptides.

■ ASSOCIATED CONTENT

Supporting Information. More characterization results of POM, DSC, and electrooptical measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) **1** (plus two molecules of pentafluorophenol) crystallizes in the monoclinic system, space group $P2_1$, unit cell edges $a = 8.329(4)$ Å, $b = 12.980(4)$ Å and $c = 12.873(7)$ Å, unit cell angles $\alpha = 90°$, $\beta = 94.53(5)°$, and $\gamma = 90°$, cell volume $V = 1387.5(12)$ Å^3, formula units per cell $Z = 4$, calculated density ρcalc = 1.538 g cm^{-3}, reliability index $R1 = 0.0547$ [intensity $I > 2\sigma(I)$], and spectral line λ(Mo Kα) = 0.71073 Å. Standard errors in the last decimal place are given in parentheses. Details of the X-ray structure determination are available from the Cambridge Crystallographic Data Centre (CCDC 787103).
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Supporting Information

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

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1. Thermal Phase Transitions

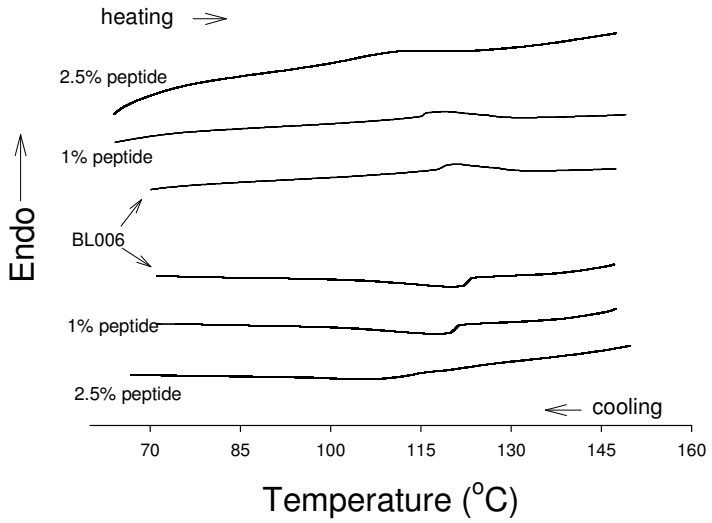

Figure S1 DSC heating and cooling curves of pure nematic liquid crystal BL006 and its mixtures with 1% and 2.5% of peptide. As a result of the reduced propensity for intermolecular stacking, the cyclopeptide has a good solubility in the used nematic LC, BL006 (Merck). This can be noticed from the DSC 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

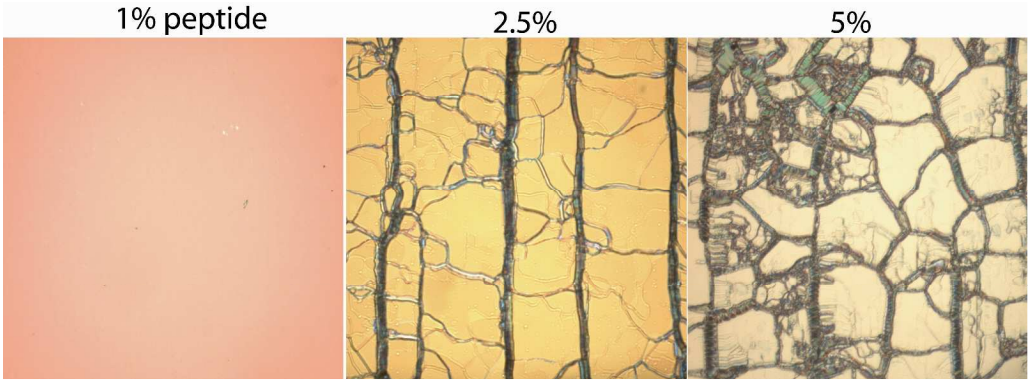

Figure S2 Polarizing optical microscope images at room temperature for BL006 doped with 1%, 2.5% and 5% of peptide, respectively. The mixtures were placed in a parallely-rubbed liquid crystal cell (10 μm gap) and slowly cooled from 130 ^{o}C (isotropic phase) to room temperature at a cooling rate of 0.2 ^{o}C/min (image size: 425μm × 425μm). 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 ^{o}C/min) from the isotropic state (130 ^{o}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

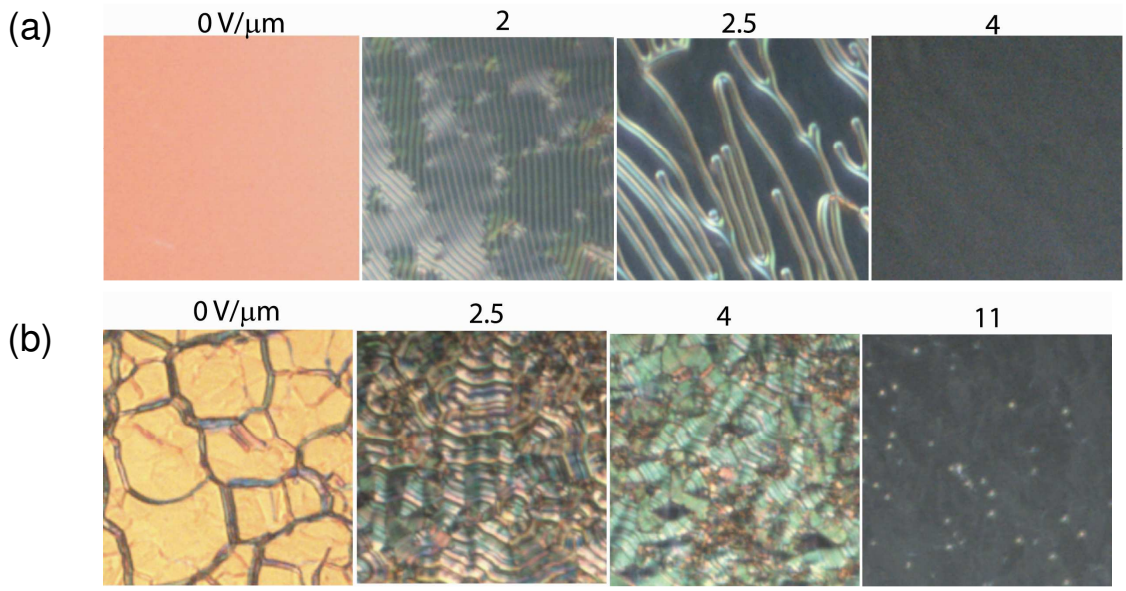

Figure S3. POM images (84μm ×84μm) recorded for BL006 containing (a) 1% and (b) 2.5% of peptide at indicated voltages. The network of defects affects the transition from the planar to the homeotropic texture.

4. Comparison with a Commercially Available Chiral Dopant

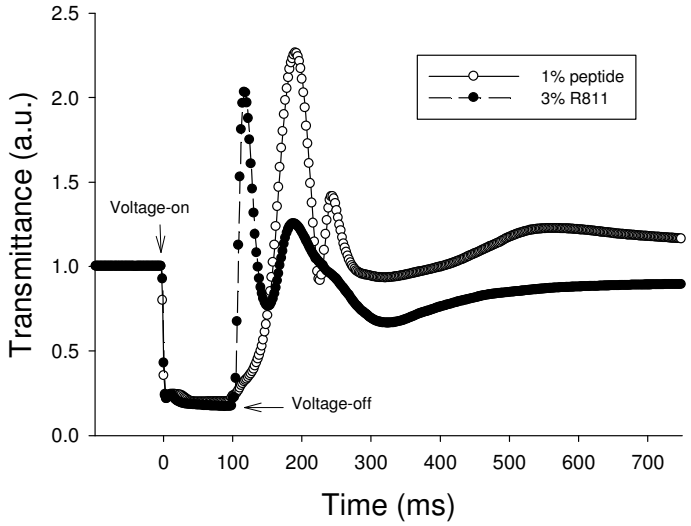

Figure S4 Transmittance change in response to one square-wave electric pulse of 100 ms (5 V/μm at voltage-on and 0 V at voltage-off) for BL006 doped with, respectively, 1% of peptide and 3% of R811 (a chiral dopant from Merck). The mixtures were placed in a parallely-rubbed liquid crystal cell (10 μm gap) and slowly cooled from 130 ^{o}C (isotropic phase) to room temperature at a cooling rate of 0.2 ^{o}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

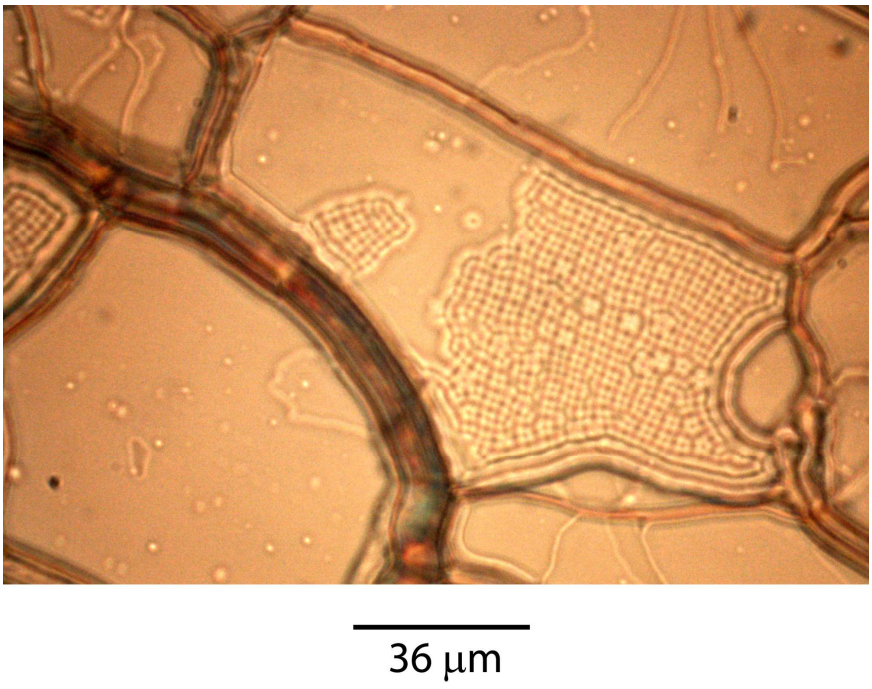

Figure S5 Polarizing optical microscope image showing regions with a square-lattice pattern, obtained with BL006 doped with 5% of peptide, slowly cooled from 130 ^{o}C to room temperature (cooling rate: 0.2 ^{o}C/min) in a parallely-rubbed liquid crystal cell (10 μm gap). The aggregates of the cyclopeptide 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

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(2) Kang, S.-W.; Chien, L.-C. *Appl. Phys. Lett*. **2007**, *90*, 221110.