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Dynamic Spirals of Nanoparticles in Light-Responsive Polygonal Fields

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Nanoparticles tend to aggregate in an uncontrollable fashion once integrated into soft matter and consequently, self-assembling nanoparticles into large-scale, regular, well-defined patterns remains an ongoing challenge towards the design and realization of smart hybrid materials. The patterns of nanoparticles that have been reported in liquid crystals are static so far, and this lack of responsiveness extends to assemblies of nanoparticles formed in topological singularities and other localized structures of anisotropic matter. Here, we demonstrate the realization of light-responsive spirals of gold nanoparticles, by using a templating strategy that is common in the biological world. Specifically, we use polygonal fields of liquid crystals that incorporate molecular photo-switches in their composition, as light-responsive chiral templates. We also show that light modifies the period of the dynamic spirals of nanoparticles. These results confirm that using chiral liquid crystals as dynamic templates constitutes a versatile strategy towards soft photonic nanomaterials, and we anticipate that the possibility to control the period of the nanoparticulated pattern can find potential applications in the field of plasmonic sensing.
Promoting the self-assembly of nano-objects into larger, functional, dynamic materials in which the size-related properties of these nano-objects can be preserved, enhanced and eventually controlled has become a contemporary field of investigations.\textsuperscript{1-6} Living systems offer compelling evidence that multiscale, sophisticated and stimuli-responsive architectures can be built simply by letting their smallest parts self-organize, as dictated by their intrinsic properties. In particular, the templating of micro- and nano-inclusions to form hybrid materials is a well-known strategy employed by nature,\textsuperscript{7,8} that has inspired the realization of hybrid optical materials\textsuperscript{9-12} and other synthetic functional materials inspired from the natural world.\textsuperscript{13-15}

In designing and realization of soft and responsive nanomaterials, taking advantage of the long-range order of liquid crystals is a valuable approach to achieve templated self-assembly.\textsuperscript{16} In particular, the supramolecular helices found in cholesteric liquid crystals are excellent candidates for the templated self-assembly of nano-objects because they combine long range ordering with mobility at the molecular level.\textsuperscript{17,18} They also display a rich range of helix-based textures that can be used as templates: oily streaks, fingerprints, grids, fan-shaped focal conics, Grandjean steps and many more.\textsuperscript{19} While dispersions of micro- and nanoparticles in chiral liquid crystals have been described,\textsuperscript{20} most investigations of self-assembled patterns are restricted to colloidal particles or to the formation of two-dimensional architectures from particle-like structures.\textsuperscript{21} Once incorporated in liquid crystals, nanoparticles form aggregates that fail to mirror any liquid-crystalline organization,\textsuperscript{22-32} except for one series of investigations templating the self-assembly of metallic nanoparticles with cholesteric fingerprints.\textsuperscript{33,34} In a few examples, the shape,\textsuperscript{22-24} orientation\textsuperscript{22-24} or the pattern geometry\textsuperscript{32} of larger aggregates were found to be dependent from a liquid crystalline environment, while bulk liquid crystals doped with nanoparticles are known to reorient under an electric field\textsuperscript{35} and light.\textsuperscript{36}
As an alternative to bulk systems, localized topological structures have been used as energetic traps for nanoparticles, in a variety of chiral and non-chiral liquid crystals, ranging from nematic to cholesteric droplets, blue phases, smectic films, liquid crystal colloids and liquid crystals in toroidal geometries. Arrays of topological structures carrying trapped nanoparticles were reorganized by driving each of the topological elements individually, but precise control over such topological structures in dynamic liquid crystals remains unaccounted for. The hybrid liquid-crystalline materials reported so far have shown limited possibilities for structural switching by an external stimulus. By contrast, we demonstrate dynamic spirals of gold nanoparticles, that are formed by the templating effect of polygonal fields of light-responsive liquid crystals. We show that the period of these dynamic spirals of nanoparticles can be tuned by irradiation with light.

Our system features the polygonal field that is formed by chiral nematic liquid crystals when their planar alignment is promoted in the bulk, whereas they orient perpendicularly at the free interface with air, so that their helix-based organization transforms into a polygonal texture near the interface. In two dimensions, microscopy images show fields of polygons, and in three dimensions, this geometry corresponds to patterns of double spirals that lie on surface of convex cones. Polygonal patterns are known to behave as a multiwavelength micro-mirrors, in which the intrinsic helical organization of polygonal fields determines the spatial intensity distribution of the reflected light depending on its wavelength, as seen in biological materials such as the chitin-based cuticle of beetles and helicoidal cell-wall architecture in fruits. Polygonal patterns in soft matter also show potential as materials for trapping nanoparticles and living cells.
Three glass-forming cyclic siloxane liquid crystals were designed and synthesized to be used as templates for nanoparticles (Figure 1a). These materials can be stabilized by simple thermal quenching below the glass transition temperature, which allows performing structural investigations by scanning electron microscopy (SEM). As a photo-switchable dopant we use a derivative of isosorbide acid (Sorb, Figure 1b) that undergoes E-Z isomerization under irradiation with UV light. Sorb is known to induce large changes in the liquid crystal helix under illumination. The octanethiol-functionalized gold nanoparticles were mixed with the liquid crystals at a concentration of 1 wt% (Figure 1c). The preparation of the hybrid light-responsive materials was optimized to promote the self-assembly of gold nanoparticles in the polygonal texture (Figure 2a,b).

Figure 1. Chemical structures and properties of the components. a) Cyclic siloxanes CLC15, CLC35 and CLC50 and their physical properties. b) Photo-switchable chiral dopant Sorb. c) Thiol-covered gold nanoparticles and associated image obtained by transmission electron microscopy.

The nanoparticles were first incorporates in the siloxane with the highest glass transition temperature (CLC50). From the hybrid liquid crystal, a polygonal texture was formed after ~30 min of heating at 120°C, which is a typical annealing temperature for cyclic
siloxanes.\textsuperscript{33,34} However the polygonal pattern started collapsing after two hours, and eventually disappeared entirely. This temperature-induced collapse is a consequence of distortions that penetrate deeper into to bulk of the liquid crystal as annealing proceeds, which also means that the inclination of the helical axis increases continuously, until it comes close to parallel to the surface, and eventually the polygonal texture disappears. At lower temperatures, the polygonal field remains stable for up to 16 hours, which is close to the annealing time that is typically necessary for nanoparticles to organize in liquid crystals.\textsuperscript{33,34} However, only large aggregates of nanoparticles were formed at the end of the process (Figure S1a,b), likely because CLC50 is very viscous at temperatures that are so much below the temperature where it becomes an isotropic fluid. The viscosity limits the mobility of the nanoparticles and thus prevents their self-assembly.

![Image](image_url)

**Figure 2.** Nanoparticles self-assembly in the polygonal texture of the hybrid films. a - b) Polarized optical micrographs of the same area of polygonal field in chiral liquid crystal CLC15 in transmission and reflection modes, correspondingly. c - d) SEM micrographs, c)
Double spiral pattern in chiral liquid crystal (CLC15 40% + CLC35 60%), which is more stable against the electron beam compared to CLC15 due to the higher glass transition temperature. Each double spiral corresponds to a single polygon in the image by optical microscopy. These patterns are formed by cholesteric liquid crystals, in the absence of any metallic nanoparticles. d) Polygonal field in non-photoresponsive CLC15, in the presence of nanoparticles.

Next we used a liquid crystal with a longer helical pitch (CLC35), because the ratio between the bulk free energy and the surface energy theoretically depends on the helical pitch. The stability of the polygonal pattern was indeed improved, and long chains of nanoparticles were found to be occasionally nested in the periodic modulation of the polygonal texture (Figure S1c,d). We thus concluded that a liquid crystal with an even longer helical pitch would lead to the formation of well-defined patterns of nanoparticles.

When using a long-pitch liquid crystal with a low isotropic temperature transition (CLC15), we found that the nanoparticles self-assemble on a large scale by truly mimicking the organization of the polygonal field in which they form spiral patterns. We found large-scale patterns of nanoparticles nested in a network of double spirals, which we evidence by using SEM with a detection mode involving high efficiency secondary electrons that allows localizing the nanoparticles and visualizing the polygonal pattern with the same measurement (Figure 2c). Mostly the pattern involved ensembles of ~20 nanoparticles, although larger aggregates were observed occasionally (Figure S2). The nanoparticles patterns are characterized by a well-defined organization that spreads over hundreds of micrometers – evidence for such a long-range order is unprecedented (Figure 2d). We note that besides featuring double spirals on a scale of ~10–20 μm², larger circle-like structures of ~30–40 μm² are also formed (Figure S3). The coexistence of these patterns in the same large-scale
organization of nanoparticles adds to the richness of the system, with future perspectives to switch between different structural elements under irradiation with light.

In terms of mechanism, we hypothesize that the octanethiol-covered nanoparticles, which promote perpendicular anchoring of liquid crystal molecules, are capable to nucleate point topological defects, thus generating elastic forces that lead to the nanoparticles self-assembly into chains. These chains preferably locate close to the energetically favorable regions, which correspond to areas where the liquid crystal molecules are preferentially oriented parallel to the hybrid film surface, while perpendicular boundary conditions dominate at the vicinity of the siloxane-air interface. The nanoparticle network of double spirals is formed by following these locations in the polygonal texture.

The polygonal patterns respond to irradiation with light – provided that irradiation occurs at higher temperatures, where the liquid crystals are not in their glassy state. The photo-isomerization of the molecular switch decreases its molecular anisotropy and thus its helical twisting power, and consequently, the tightness of the helix-based hybrid material is increased (Figure 1b). The light-induced pitch modification of the liquid crystal (Figure 3a) has consequences on the geometry of the spirals of gold nanoparticles. The double spiral patterns of nanoparticles follow the light-induced transformations of the polygonal field (Figure 3b-g) and namely, irradiating the nanoparticle-doped photo-responsive films modifies the distance between the spiral arms, as the periodic modulation in these double spirals is directly related to the period of the cholesteric helix. The narrowing of the double-spiral nanoparticles patterns is not always very visible in the SEM images because the show two dimensional projections of three dimensional cones, and thus the decrease in the period of the fingerprint spirals shows in two dimensions only when the polygonal field is composed by uniform cones of similar size and height. Besides, the chains of nanoparticles become thicker as the UV
irradiation times increase (Figure 3f). We attribute the thickening of the network lines to the necessity to heat the samples out of the glassy state during exposure to light, which increases the mobility of the nanoparticles in the template.

**Figure 3.** Light-induced structural modifications. a) Shift of the selective reflection band for planar films of CLC15 after doping with Sorb and gold nanoparticles before UV irradiation and after increasing exposure times. Insets: optical microscopic images of four non-irradiated planar films. The maximum of the selective reflection $\lambda_R$ is determined from the Lorentz fit of each absorption spectrum. b - g) SEM micrographs of nanoparticle patterns in the photoactive
cholesteric liquid crystal (CLC15 + Sorb 0.6 wt%) exposed to UV light for b) 0 s, c) 15 s, d) 30 s, e) 120 s, f) 240 s, g) 600 s.

Extending this templating approach to non-spherical or larger nanoparticles is likely to support new developments towards soft photonic nanomaterials with optical characteristics that are controlled from the molecular level upwards, as the characteristics of the surface plasmon resonance depend both on the size and on shape of nanoparticles.\textsuperscript{51} Moreover, the design of uniform polygonal fields, with liquid crystals that undergo large pitch changes under illumination, will enhance the amplitude light-induced reorganizations. Finally, using lyotropic liquid crystals as templates for bigger nanoparticles will broaden the field further, as the size of the defect cores that hold the nanoparticles in the vicinity of the interfacial zone reaches several dozens of nanometers in these materials,\textsuperscript{52} whereas it is \(\sim 10\) nm only in thermotropic liquid crystals.\textsuperscript{53} Further studies on the development of dynamic spirals of nanoparticles will be aimed both at understanding the multistep mechanism of nanoparticles self-assembly in polygonal fields, and in improving the characteristic properties of these polygonal templates, such as realizing a uniform field of photo-controllable polygons, for a wide range of helical pitches.

In conclusion, we demonstrate a versatile and tunable platform that directs the self-assembly of gold nanoparticles into well-defined double spirals that lie on convex cones, in polygonal fields of cholesteric liquid crystals. The distance between the spiral arms of the patterns of nanoparticles can be controlled by light, because the periodic modulation in the double spirals directly relates to the period of the cholesteric helix. This hybrid system features dynamic amplification of chirality across length scales, features the possibility to reconfigure a long-range network of nanoparticles with light, and demonstrates a true nanoparticle self-assembly in chiral soft matter – meaning that the nanoparticles follow the periodic helical modulation of
the ordered cholesteric arrangement, instead of being trapped in topological defects or other regions of molecular disorder. This bio-inspired templating approach holds potential for the future of hybrid materials because there is no conceptual restriction to extend it to a large variety of nano-objects, including platelets,\textsuperscript{54} plant viruses\textsuperscript{55} and other nanocontainers.\textsuperscript{56} Directing the self-assembly of metallic nanoparticles with chiral liquid crystals will give rise to periodically structured hybrid materials that comply with the definition of metamaterials, with potential applications to chiral sensors, tunable optical connectors for the long-distance transportation of light, and other light-based technologies.

**Experimental Section**

*Materials:* The cholesteric liquid crystal siloxanes CLC15, CLC35, and CLC50 were synthesized by Synthon. Before use, we performed an additional purification procedure that involves dissolution in acetone under sonication, filtration of the clear solution on paper and precipitation by addition of methanol, centrifugation of the cloudy precipitate for 5 min at 5000 rpm, and removal of the solvents mixture. The procedure was repeated a few times, and traces of solvents were eventually removed under vacuum to yield a sticky oil.

The photo-switchable chiral dopant Sorb (2,5-bis(4-methoxycinnamoyl)-1,4;3,6-dianhydro-D-sorbitol) was synthesized by following a reported protocol.\textsuperscript{49} Gold nanoparticles of 2–4 nm in diameter and functionalized with octanethiol were purchased from Sigma-Aldrich. All components were soluble in toluene.

*Doping of liquid crystal siloxanes:* The siloxanes were heated up to 75 – 120 °C depending on the temperature of their phase transition to the isotropic state. Then, the photo-switchable chiral dopant was added (Section S4). Next, an appropriate volume of gold nanoparticles in suspension was added, as well as 3 mL of toluene. The thus prepared solution was sonicated
for 1 hour in the ultrasonic bath, and then placed in a flask at 140 °C until all the toluene was evaporated. The procedure yielded a hybrid, cholesteric liquid crystal.

**Planar photo-responsive films:** Planar cells of the nominal thickness of 15 µm were purchased from E.H.C. All cells were filled at 65 – 75 °C, kept for 20 min at this temperature to reach thermodynamic equilibrium, and slowly cooled down to room temperature.

**Hybrid photo-responsive materials:** Two clean glass substrates and a flask containing the siloxane were heated up to 65 – 75 °C. Two pieces of 6 µm Mylar spacer were placed on the first glass substrate at a distance of about 2.5 cm. A drop of cholesteric mixture was placed in the center. The second glass substrate was placed on top of the droplet. When irradiation was required, the cell was exposed to UV light at 65 – 75 °C, *i.e.* in the mesoscopic state of chiral liquid crystal. The cell was kept on a hot plate for a few minutes under mechanical pressure created by a metal cylinder that was preheated to the same temperature. The color optical reflection appearing from the cell indicated the planar liquid crystal arrangement introduced by shearing. The cell was then placed on a metal plate at 4 °C, down to the glassy state. CLC15-based cell was additionally transferred to the freezer at – 22–25 °C to prevent the liquid crystal from sticking on the glass slide, when opening the sample. After four hours in the freezer, the top glass of the cell was removed. The resulting hybrid film was then annealed, and a polygonal field was formed to satisfy the perpendicular boundary conditions at the free interface with air.

Our first SEM observations of the annealed films based on CLC15 revealed that the nanoparticles locate preferably well below the open surface, in the bulk of the cholesteric layer. The absence of nanoparticles at the free interface likely stems from the fact that, at the
stage of cell preparation, the nanoparticles avoid the interface with the glass substrate, because of the perpendicular anchoring conditions promoted by the thiol coating.\textsuperscript{50} We thus adjusted the procedure by removing a thin slice away from the open surface with a blade, before annealing. After annealing, the patterns of nanoparticles were thus located at the air interface instead of being buried in the bulk.

**UV light source:** UV exposing ($\lambda = 365$ nm) was performed using a Hönle bluepoint LED lamp. All cells were placed at $\approx 6$ cm from the exit pupil of the optical fiber. The intensity of the UV lamp was set at 80% level from the maximum intensity measured as 170 mW cm$^{-2}$. UV irradiation of the photo-responsive siloxanes was carried out at 65 – 75 °C to ensure that the material is in the mesoscopic liquid crystalline state.

**Structural characterization:** The liquid crystal textures were imaged with an Olympus BX-51 polarized optical microscope. The UV-visible spectra were acquired using an Ocean Optics USB2000+ spectrometer. SEM images were taken by using a HE-SE2 detector at low accelerating voltage of the electron beam, to avoid damaging the films. The films were not coated with any metallic layer, because heating during the coating deposition destroyed the polygonal texture.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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References


The long range organization of nanoparticles is templated effectively by double spirals that lie on the convex cones of polygonal fields of chiral liquid crystals. Moreover, the distance between the spiral arms of nanoparticles can be controlled by light. This approach towards dynamic, long-range and self-assembled patterns of metallic nanoparticles features chiral amplification across length-scales and holds perspective for advanced hybrid nanomaterials.

**Light-responsive spirals of nanoparticles**

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**Dynamic Spirals of Nanoparticles in Light-Responsive Polygonal Fields**
Supporting Information

Dynamic Spirals of Nanoparticles in Light-Responsive Polygonal Fields

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1. Nanoparticles aggregation in the hybrid CLC50-based and CLC35-based films
2. Nanoparticles self-assembly in the hybrid CLC15-based films
3. Well-defined nanoparticle patterns in the hybrid CLC15-based films
4. Optimization of Sorb concentration in hybrid CLC15-based materials and light irradiation conditions
1. Nanoparticles aggregation in the hybrid CLC50-based and CLC35-based films

![image](image1)

**Figure S1.** Enormously large aggregates of nanoparticles in the hybrid CLC50-based films formed after a) 7 hours of annealing at 90°C and b) 16 hours of annealing at 65°C. c) Rare long chains of nanoparticles formed together with aggregates in the hybrid CLC35-based film after 13 hours of annealing at 110°C while d) only the moderate aggregates of nanoparticles were found in the same hybrid CLC35-based film after 16 hours of annealing at 80°C. Charging effect appears on the b), c), d) images due to the increased electron beam voltage.
2. Nanoparticles self-assembly in the hybrid CLC15-based films

![Figure S2. Nanoparticles self-assembly in the hybrid CLC15-based films. a) SEM micrographs at low and b) high magnifications. Charging effect appears in the a) image due to the increased electron beam voltage. The polygonal texture is invisible in these SEM micrographs, because they are taken by ESB detector.](image)

3. Well-defined nanoparticle patterns in the hybrid CLC15-based films

![Figure S3. Well-defined nanoparticle patterns in the thin films of photoactive cholesteric liquid crystal (CLC15 + Sorb 0.6 wt%), after it was exposed to UV light for a) 30 s, b) 240 s.](image)

4. Optimization of Sorb concentration in hybrid CLC15-based materials and light irradiation conditions

We rationalized that templating of nanoparticles requires an annealing temperature typically below the isotropization temperature of ~20°C, while the polygonal field remains stable for typically 16 hours. Next we evaluated how the chirality of Sorb influences the polygonal
texture of the CLC15. When doping with 0.75 wt%, polarized optical microscopy showed that the polygons are deformed, and a further increase in the Sorb concentration up to 2 wt% destroys the polygonal field altogether. This collapse is likely due to the unwinding of the cholesteric helix, as the liquid crystal is diluted with a chiral dopant that promotes the handedness which is opposite the handedness of CLC15. We avoided deformation of the polygonal texture by setting the Sorb concentration to a 0.6 wt% in hybrid CLC15-based materials.

The light irradiation conditions were optimized by following the selective reflection band of thin films at planar anchoring conditions in the absence of any polygonal features (Figure 3a). Doping of CLC15 with 0.6 wt% of Sorb resulted in a ~100 nm red shift of the selective reflection band due to unwinding of the cholesteric helix, while additional doping by 1 wt% nanoparticles led to a red shift in a few nanometers only, because such small nanoparticles do not dilute the chiral character much and have little effect on the cholesteric ordering.