Lasing and waveguiding in smectic A liquid crystal optical fibers

Karthik Peddireddy[a], V. S. R. Jampani[b], Stephan Herminghaus[a], Christian Bahr[a], Maruša Vitek[b] and Igor Muševič*[b]
[a] Max Planck Institute for Dynamics and Self-Organization (MPIDS), 37077 Goettingen, Germany;
[b]J. Stefan Institute, Jamova 39, SI-1000, Ljubljana, Slovenia.

ABSTRACT

We demonstrate a new sort of optical fibers, which are self-assembled from a smectic-A liquid crystal. When this liquid crystal is put in contact with water solution of surfactant CTAB, microfibers start spontaneously growing at the liquid crystal-water interface. The fibers are of very uniform diameter and can be several hundreds of micrometers long. They all have a line topological defect in the core of the fiber with a local optical axis pointing from the defect core towards the surface. The ends of the fiber are of perfect spherical shape. By doping the fibers with a fluorescent dye, we demonstrate guiding of light along the fiber. When the fiber is illuminated with pulsed light, which is absorbed by the dye, we observe Whispering Gallery Mode (WGM) lasing in a plane perpendicular to the fiber. The smectic-A fibers are soft and flexible and can be manipulated with laser tweezers demonstrating a promising approach for the realization of soft matter photonic circuits.

Keywords: polymer waveguides, microcavity devices, liquid-crystal devices, fiber optic waveguides.

1. INTRODUCTION

Nematic phase of liquid crystals is formed of rod-like molecules that by cooling down, spontaneously organize with their long molecular axis parallel to each other at a certain temperature, which is called the clearing point. Above this temperature, the nematic liquid crystal is just an ordinary liquid, while below the clearing point it exhibits anisotropic optical, dielectric, magnetic and elastic properties. Because of orientational ordering of anisotropic liquid crystal (LC) molecules, a nematic liquid crystal (NLC) is optically uniaxial material with the optical axis pointing along the direction of average molecular ordering, which is called the director, $\vec{n}$. By further lowering the temperature, the nematic phase usually spontaneously transforms into the smectic-A phase. This phase preserves the spontaneous orientational order, but the LC molecules are positionally ordered into molecular layers, called smectic layers, the layer planes being perpendicular to the director.

The birefringence of a typical NLC is of the order of $\Delta n \approx 0.1-0.2$, although NLC materials with much larger, or much lower birefringence are known as well. In addition to optical anisotropy, NLCs exhibit anisotropic material properties, such as the anisotropy of a dielectric constant, which is a tensorial quantity in LCs. The electric polarizibility of a NLC is usually larger, when measured along the long molecular (and therefore along the director), and the dielectric anisotropy could be quite substantial. The dielectric anisotropy is technologically important and is used in flat screen LCD devices to turn-on each liquid crystal pixel of the screen. Namely, when an electric field is applied to the pixel, the molecules tend to align along the field direction to minimize their electric energy. In addition to the optical and dielectric anisotropy, a NLC exhibits an orientational elasticity, meaning the liquid crystal could be elastically distorted, therefore storing the elastic energy in the deformed regions. This elasticity is a consequence of a broken orientational symmetry of the nematic phase and is technologically extremely important, as it drives each pixel on a flat LCD screen back into the equilibrium state, after the driving voltage at that pixel is switched-off.

There has been a renewed interest in dispersions of colloidal particles in the nematic liquid crystals, which could be used in various photonic applications, such as tunable 2D and 3D photonic crystals, and metamaterials. In addition to that,

*igor.musevic@ijs.si; phone 386 1 4773 572; www.softmatter.si

Liquid Crystals XVIII, edited by Iam Choon Khoo, Proc. of SPIE Vol. 9182, 91820Y
 · doi: 10.1117/12.2061303

there is a large interest in mixtures of nematic liquid crystals in liquids that do not mix with most NLCs, such as water, glycerine, different polymers, etc... Because of chemical incompatibility, NLCs readily and spontaneously form small and perfectly spherical droplets, which are internally well ordered therefore representing interesting photonic structures. It has been demonstrated that $10-30\,\mu m$ nematic droplets with radial orientation of LC molecules inside the droplet (i.e. radial structure), support Whispering Gallery Modes[1] and represent a birefringent optical microresonator. Because of the softness of NLCs and their strong response to external electric field, the spectrum of WGMs can be tuned nearly hundred times more efficiently than in solid microresonators. Lasing has also been observed from radial nematic droplets[2], and it has been shown that the lasing spectrum strongly depends on the presence of foreign molecules, floating around the microresonator. Namely, it is known that surface adsorption of foreign molecules at the surface of such a resonator, may change the internal organization of the NLC in the microresonator, therefore influencing the eigenfrequencies of WGMs. Liquid crystal droplets could therefore be used as chemical sensors, signaling the presence of target molecules by changing the lasing spectrum when these attach to the interface.

An interesting class of soft-matter microphotonic devices has been found in water dispersions of cholesteric liquid crystals (CLCs). These materials are made of chiral molecules and because of molecular chirality, they form a spontaneously twisted nematic phase in the direction, perpendicular to the local nematic director. The pitch of this helical structure depends on the strength of chirality and can be tuned chemically from UV to IR part of the spectrum. Because of the helical organization of birefringent matter, the CLC is a one-dimensional photonic crystal that strongly reflects circularly polarized light of proper handedness and wavelength. In a droplet, such a CLC spontaneously forms the onion-Bragg photonic structure, which has a photonic band gap for circular light travelling radially out of the droplet. It has been demonstrated[3] that such droplets emit laser light uniformly in all directions, making them ideal isotropic point source for potential application in display devices, holograms etc..

Quite recently, we have demonstrated the third class of microphotonic liquid crystal devices, which are optical microfibers, self-assembled from the smectic-A liquid crystal in contact with water and surfactant[4]. In this paper, we give a review of this finding and we show that there is a huge variety of optically interesting self-assembled structures in dispersions of smectic-A liquid crystals in water with added surfactant.

2. STRUCTURE AND GROWTH BEHAVIOR OF SMECTIC FIBRES

Rod-shaped organic molecules can form the smectic-A liquid crystal phase, which is a liquid possessing a combination of orientational and positional order. The orientational molecular order, caused by the tendency of the molecules to align spontaneously along a common direction, results in anisotropic properties such as optical birefringence. In addition to the orientational ordering, characteristic of the nematic phase, in the smectic-A phase the molecules arrange themselves in layers, the layer planes being perpendicular to the average direction of the long molecular axes (Figure 1, left panel). Recently, we observed that smectic-A liquid crystals can form spontaneously fiber-like structures when brought in contact with aqueous phases containing ionic surfactants.[5] Figure 1 (right panel) shows a photograph, obtained with a polarizing microscope, of the growing fibers. For our experiments, we used the common liquid crystal compound 8CB (4-octyl-4′-cyanobiphenyl), which is in the smectic-A state at room temperature, and the surfactant compound CTAB (hexadecyltrimethylammonium bromide), dissolved in water at concentrations between 10 and 100 mM.

2.1 Structure of smectic-A fibers

The photograph shown in Figure 1 (right panel) is obtained by placing a small amount of the smectic liquid crystal between two glass slides (separated by 125 μm spacers) and subsequent contacting the smectic material with the aqueous surfactant solution (which is sucked between the slides by capillary forces). In that setting, the growth of the smectic fibers proceeds in

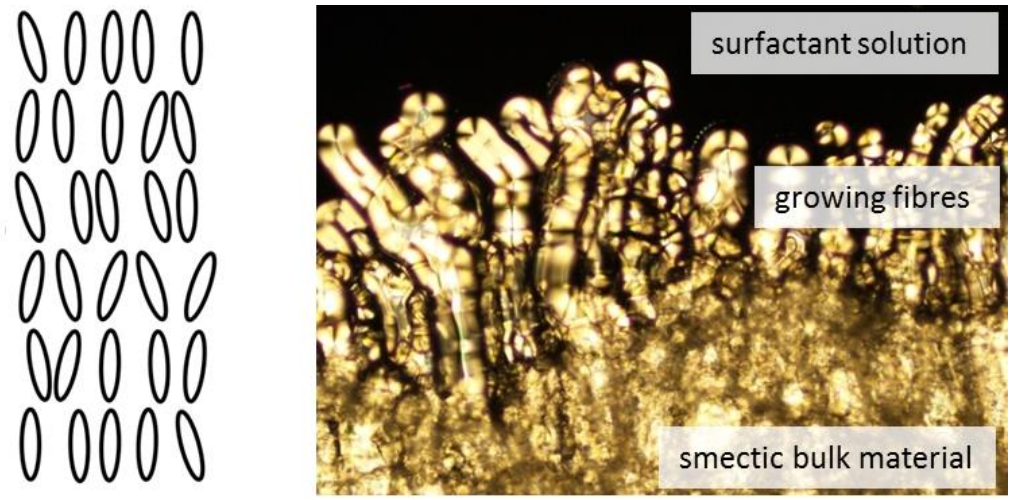

Figure 1. Left: Schematic sketch of the molecular arrangement in the smectic-A liquid crystal phase. Typical dimensions of the rod-shaped molecules (drawn as ellipsoids) are 2-3 nm in length, and 0.5 nm in width. Right: Micrograph (crossed polarizers) of smectic fibers growing from a smectic bulk phase (8CB) into an aqueous surfactant solution (concentration 27 mM CTAB). The horizontal width of the image is ≈ 1 mm.

a kind of arbitrary and uncontrolled way. It is possible to grow the fibers in a more confined environment, such as a glass capillary with a rectangular or square cross section. The confinement by the capillary guides the growth and it fixes the position of the fiber (which would otherwise freely float in the surfactant solution), thereby enabling structural studies using the method of fluorescence confocal polarizing microscopy (FCPM).[6]

For the FCPM investigations, the smectic liquid crystal is doped with a small amount of a fluorescence dye (Nile red, concentration 0.005 weigth %). The Nile red molecules possess an elongated shape and align parallel to the smectic liquid crystal molecules. If the fluorescence is excited with linearly polarized light, the intensity of fluorescence is maximum in those regions of the sample where the dye molecules (and the liquid crystal molecules) are parallel to the polarization of the exciting light. Thus, the distribution of the fluorescence intensity provides information about the local orientation of the liquid crystal molecules. In addition, the aqueous phase is doped with a different fluorescence dye (fluorescein, concentration 0.01 weight%). Since the two dyes can be excited separately, the FCPM investigations provide also information about the spatial distribution of the two different phases (the smectic liquid crystal and the aqueous surfactant solution) in our sample.

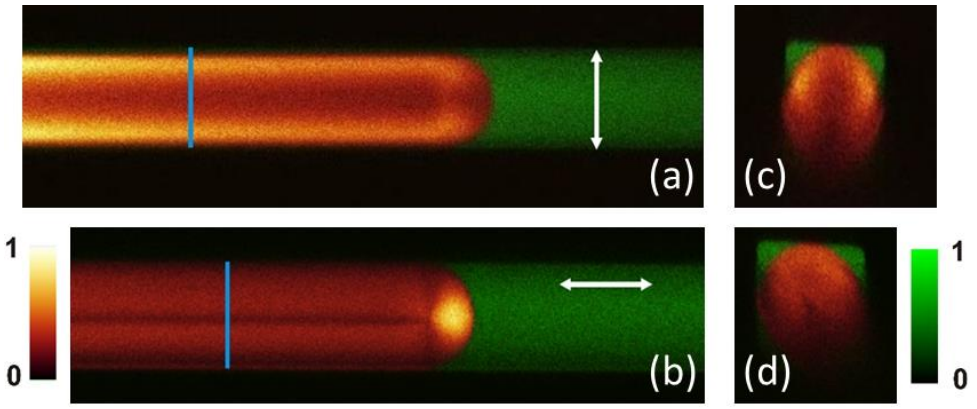

Figure 2. FCPM images of a smectic fiber confined in a glass capillary (square cross section, width 35 µm). The red color code refers to the fluorescence signal of Nile red (dissolved in the smectic compound 8CB), the green color color refers to the fluorescence signal of fluorescein (dissolved in the aqeous surfactant solution (CTAB, concentration 20 mM)). Panels (a) and (b) represent cross sections parallel to the fiber axis, obtained with two different orientations (indicated by the white arrows) of the polarization of the exciting light. The intensity distribution of the Nile red signal indicates that the smectic liquid crystal molecules are aligned perpendicular to the surface of the fiber. Panels (c) and (d) represent cross sections perpendicular to the fiber axis (along the blue lines in (a) and (b)) and demonstrate the circular shape of the cross section of the fiber in the square-shaped capillary.

Figure 2 shows FCPM images of a smectic fiber growing in a glass capillary which is filled initially with the aqueous surfactant solution. The intensity distribution of the Nile red signal indicates that the smectic liquid crystal molecules are aligned with their long axes perpendicular to the surface of the fiber. The FCPM images also show that the fiber possesses a cylindrical shape with a circular cross section and a hemispherical cap at the end of the fiber. These results lead to the conclusion of a concentric arrangement of the molecular layers around the fiber axis as sketched in Figure 3. If the fibers are grown without defects in the smectic layer structure (except the central line defect along the tube axis), the fibers possess a surface which is smooth on the molecular scale. Furthermore, since the smectic layers can be regarded as nearly incompressible, the thickness of a fiber is practically constant.

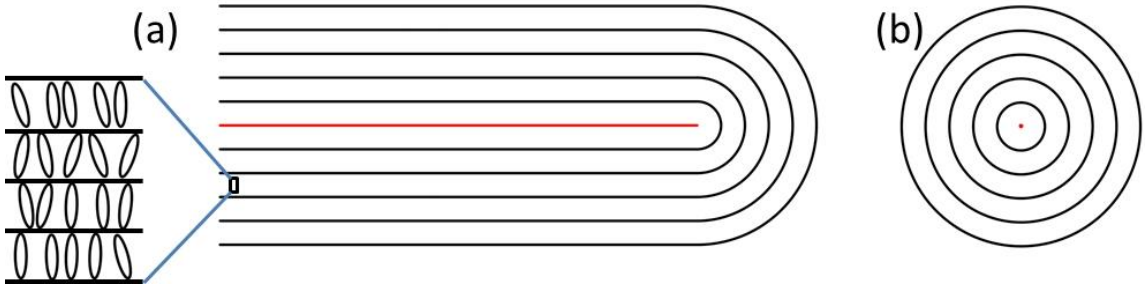

Figure 3. Schematic cross sections of a smectic fiber parallel to the fiber's axis (a) and perpendicular to the fiber's axis (b), illustrating the arrangement of the molecular layers in the fiber. The black lines indicate the arrangement of the layers, the red line corresponds to a line defect along the tube axis where the smectic order breaks down.

2.2 Growth behavior and variety of smectic-A fiber-like structures grown in CTAB/water solution

The detailed mechanism of the growth of the smectic fibers is still to be clarified. However, we found that the variation of the surfactant concentration in the aqueous phase, in which the fibers are grown, enables to some extent the control of

their dimensions. The left panel of Figure 4 shows the length of growing fibers as a function of time for two different surfactant concentrations in the aqueous phase. Within a few minutes, the fibers reach a length L of several hundred micrometres, following a $L \sim \sqrt{t}$ relation.

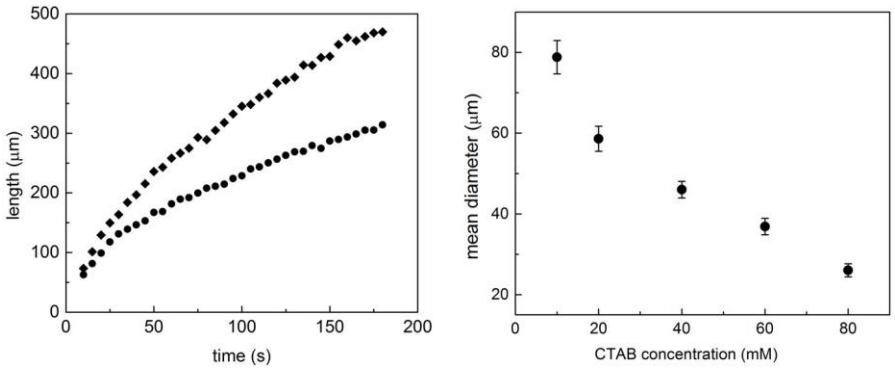

Figure 4. Left: Length of the growing smectic fibers as a function of time for two different surfactant concentrations in the aqueous phase, ♦: 10 mM, ●: 60 mM. Right: Mean diameter of the smectic fibers as a function of the surfactant concentration in the aqueous phase.

Counterintuitively, increasing the surfactant concentration appears to slow down the growth of the fibers, at least when the length is taken as a measure of the fiber growth. As shown in the right panel of Figure 4, increasing the surfactant concentration results also in a decrease of the diameter of the fibers and this behavior is accompanied by an increase of the number density of the fibers. In aqueous phases with very high surfactant concentrations, it is possible to obtain fibers with a diameter of only a few micrometres. One can manipulate the smectic fibers in several ways using optical tweezers. More details can be found in our recent paper.[7]

In the experiments having a smectic-A droplet in contact with water solution of CTAB, smectic-A fibers usually stay connected to the LC droplet, but are otherwise not fixed (to the surface, for example). They are at all times free to grow, move and undergo some shape changes. In fact, observing the fibers growth under a microscope reveals very vivid and perpetuating movement of the tangle of micrometer diameter fibers, caused by the smectic-A interface instability. By using the IR laser tweezers, one is able to grab and manipulate the fibers, because it has higher refractive index than water. Furthermore, by illumination with a pulsed laser, we can induce structural instabilities that cause the fiber to start ejecting very thin fibers, or to change the fiber's surface from smooth to wrinkled.

Figure 5 shows a snapshot from a video-movie, which shows that the fiber became unstable after being exposed to the pulsed laser. At the beginning, we had a fiber that was uniform in diameter. After illuminating it with a strong pulsed doubled Nd:YAG laser, a somewhat thinner fiber started to emerge from the fiber's end and the primary fiber shortened. In less than a minute, some wider areas appeared along the fiber, which can be considered as "spherical containers", indicating a kind of pearling instability. The picture also shows the coexistence of smectic fibers of different diameters, with thinner fibers forming Y-junctions. This experiment was performed in 100 mM CTAB solution in an 85 μm thick glass cell.

Instead of fibers of perfect cylindrical shape, sometimes other interesting structures can be spontaneously formed under the same chemical conditions, as shown in Figure 6. Figure 6a shows a fiber-like structure showing the areas, where the width of the structure is increased and the core defect line transforms into a kind of a loop or a defect wall. Panel (6b) shows a picture of a Y-branched symmetric structure with an interesting defect configuration in the cross-section of fiber-like

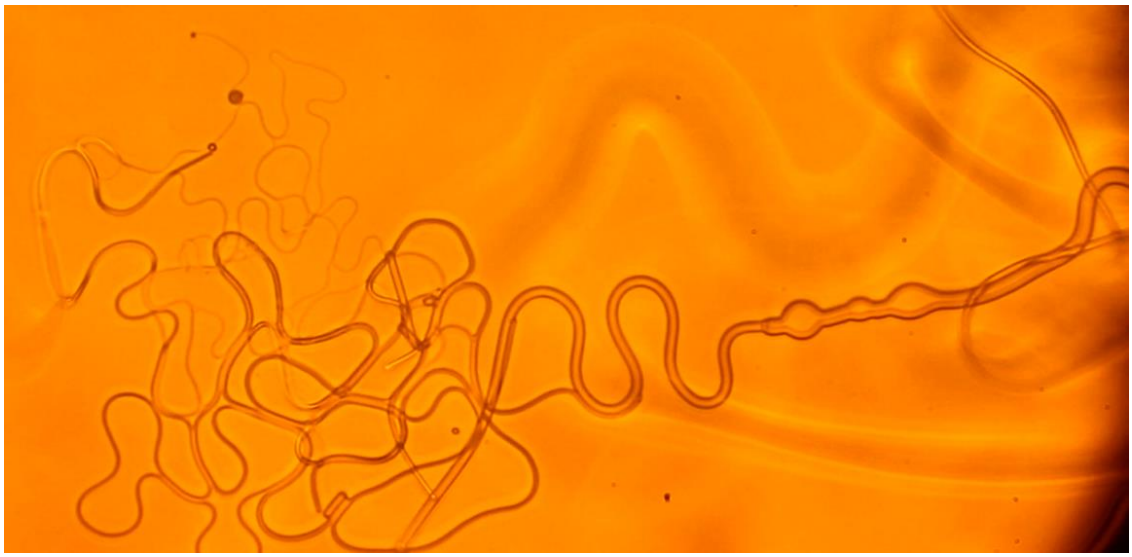

Figure 5. Snapshot from a video-movie, demonstrating the instability of the smectic-A fiber, caused by illumination with a pulsed doubled Nd:YAG laser. After having been exposed to the illumination, the fiber started to form wider areas (on the right) and a thinner fiber started to emerge from the fiber's end, moving towards the left side. The primary fiber shortened on this account, whereas the overall structure became longer and thinner. We can also see that thinnest fibers adhere to each other and form Y-junctions (left).

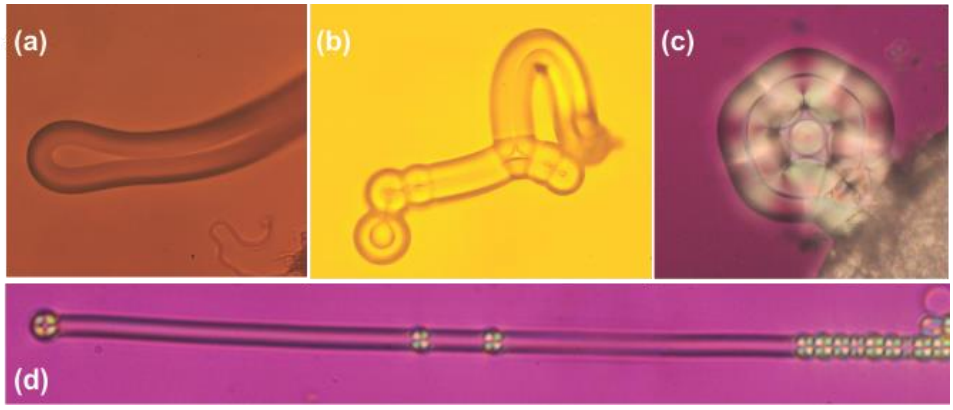

Figure 6. Variety of self-assembled smectic-A structures. (a) Fiber-like structure, where in some areas the width of the fiber is increased and the defect line in the center is deformed. (b) Fiber-like branched structure that got separated from the bulk LC droplet. In the junction region an interesting defect configuration appears. (c) An exotic smectic-A, torus-like structure with a five-fold symmetry. (d) Smectic fiber that contains bead-like structures and ends with one bead. Such beads form on the fiber spontaneously. All experiments were done in 100 mM CTAB water solution in a 85 μm thick cell.

structures that is yet to be explained. Sometimes more exotic circular structures are spontaneously formed, such as a regularly deformed torus with five-fold symmetry, as shown in Figure 6c. We also observed fibers that end with one or several bead-like structures, shown in Figure 6d. These "beads" are radial spherical inclusions in a cylindrical fiber and can form spontaneously anywhere on the fiber and can freely move along the fiber. By careful studying of a variety of

different structures that can form from the smectic compound in CTAB/water solution, a better understanding of the growth mechanism should be obtained.

Finally, in many cases we obtain several hundred of micrometers long and extremely uniform smectic-A fibers, as shown in Figure 7. This clearly demonstrates high potential of smectic-A fibers for photonic applications.

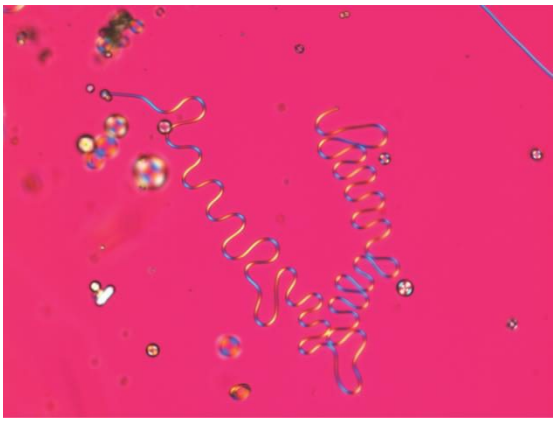

Figure 7. Very long and very uniform smectic-A fibers can be grown in water-CTAB solution.

3. WAVEGUIDING AND LASING FROM SMECTIC-A FIBRES

Because of their perfect cylindrical shape, very uniform diameter and defect-free internal structure, the smectic-A fibers are ideal candidates for optical waveguides and optical microresonators for various applications. Each concentric layer of this material has the local optical axis oriented in the radial direction of the fiber. This means that the electromagnetic wave, propagating along the fiber and polarized in a radial direction, senses the extraordinary refractive index, which is quite high. If the fiber is surrounded by a low-refractive index material, such as water, the conditions for total internal reflection will be satisfied and the smectic fiber should guide light. To study the waveguiding and lasing properties of the fibers, the experiments were performed on an inverted microscope (Nikon Eclipse, TE2000-U), using the set-up described elsewhere. The fibers were kept in glass cells (thickness 100 μm) freely floating in the aqueous surfactant solution in which they were grown. The setup is a combination of an infrared fiber laser tweezers operating at 1064 nm (Aresis) and a continuous Ar^+ laser tweezers operating at 514 nm using a 60 x high numerical aperture objective. The infrared laser tweezers were used to manipulate the smectic fibers in the aqueous environment.

Waveguiding properties of the smectic-A fibers are presented in Figure 8. To study propagation of light in fibers, the tightly focused beam of the continuous Ar^+ laser tweezers was directed to one end of a fiber. Because the fibers were previously doped with fluorescent Nile red molecules, light propagation inside the fiber was easily monitored by observing fluorescent light emitted from the fiber. In panel 8a the tweezers was positioned at the spherical cap of a rather thick smectic-A fiber. One can clearly see propagation of light, reflected from the inner side of the spherical cap, and spiraling along the fiber-water interface due to total internal reflection. To analyze optical losses due to structural imperfections in the fiber, a thinner fiber was selected, as shown in Figure 8b. When light is propagating along the interior of such a fiber, it is uniformly illuminated by the leaking fluorescent light. Because the intensity of this fluorescent light is proportional to the guided light, we could qualitatively determine losses in fibers over hundreds of micrometers length. The intensity of the leaking fluorescent light along the tube's length is shown in Figure 8c for two different polarizations. One can see that light losses are negligible over fiber's length of ~100 μm.

Because of their perfect cylindrical shape, smectic-A fibers are ideal candidates for laser resonators. In such a resonator, light can circulate inside the fiber in a plane perpendicular to the fiber's axis by consecutive total internal reflections at the smectic-A-water interface8. These resonances are therefore conceptually similar to WGM resonances in spherical

microresonators1, with the difference that in a cylindrical resonator the modes are different from spherical eigenmodes inside the dielectric sphere.

To study the lasing properties of the fibers, lasing was initiated by illuminating the dye-doped fibers with a pulsed laser (Nd: YAG 532 nm, Alphalas, Pulselas-A-1064-500) with a 100 Hz repetition rate, a pulse length of 1 ns and a maximum pulse energy of 10 μJ. An imaging spectrometer with a 0.05 nm resolution (Andor, Shamrock SR-500i) was used to measure the fluorescence and lasing spectra of the fibers, and a cooled EM-CCD camera (Andor, Newton DU970N) was used to take photographs of the fibers. Figure 9 shows photomicrographs of a 50μm diameter smectic-A fiber, doped with fluorescent dye Nile red, and illuminated with pulsed doubled YAG light. At low pump intensity (Figure 9a), only

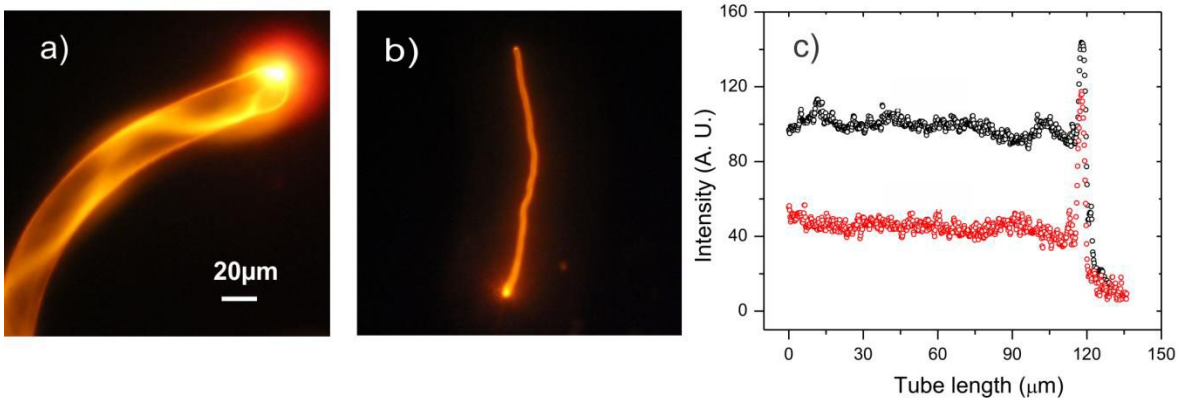

Figure 8. Waveguiding of light in smectic-A fibers of 8CB liquid crystal. (a) Spiraling of light due to total internal reflection in a large-diameter smectic-A fiber. (b) A thinner fiber is completely illuminated with guided light. (c) Fluorescent light intensity, measured at different positions along the fiber. Data are shown for two different polarizations of the excitation light, higher intensity is obtained for polarization perpendicular to the fiber's axis.

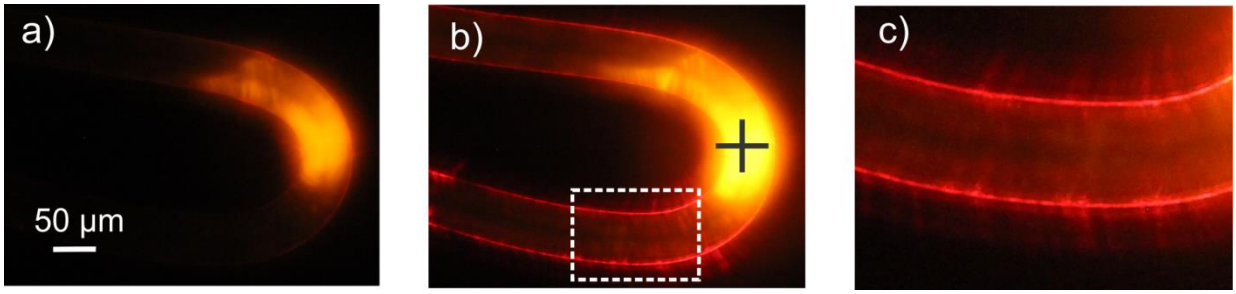

Figure 9. Lasing from smectic-A fibers. (a) The fiber, grown from 8CB liquid crystal, is doped with fluorescent dye Nile red and illuminated with the green pulsed light from a doubled YAG laser. Fluorescence is seen. (b) After increasing the level of the green pumping light, the fluorescence is enhanced, and above the threshold, the fiber starts emitting nearly monochromatic light all along its interface. (c) Enlarged dotted area from panel (b) clearly shows laser light emission from the water-liquid crystal interface.

localized fluorescence of the Nile red dye is observed. By increasing the intensity of the pumping light, at some level the smectic-A-water interface starts emitting very intense and monochromatic red light, as shown in Figure 9b. The interface is emitting reddish light over substantial separations from the center of the pump light, indicated by the cross in Figure

9b. By enlarging the area around the water-liquid crystal interface, one can clearly observe interference speckles emanating from the interface, as shown in Figure 9c. This is characteristic of laser light emission from the interface. The analysis of light, emitted from the interface, reveals several sharp laser lines, separated by 5-10 nm, which is characteristic of a WGM spectrum. The threshold for lasing is quite low and is of the order of 0.1 mJ/cm^2. This is several times lower threshold compared to the lasing in spherical micro-resonators self-assembled from a nematic liquid crystal[2].

4. CONCLUSIONS

It is quite surprising that excellent optical waveguides could be grown from smectic liquid crystals, although their layered smectic structure suggests possible existence of fiber-like or tubular-like objects, where the smectic layers are rolled up in a series of concentric smectic layers. It is also surprising how perfectly the smectic liquid crystal fills both ends of the cylindrical fiber with two perfect hemispherical caps. However, it seems that there are even more surprises in these dispersions, because we observed objects with many different shapes and topologies, yet to be explored. There are certainly several very interesting challenges in this direction, and the priority is to develop new methods for the shape-stabilization of fibers and their controlled growth. Successful realization of these challenges would certainly made a strong contribution towards rapidly developing field of soft matter photonics.

REFERENCES

[1] Humar, M., Ravnik, M., Pajk, S. and, Muševič, I., "Electrically tunable liquid crystal optical microresonators," Nat. Photonics 3, 595-600 (2009).

[2] Humar, M. and Muševič, I., "Surfactant sensing based on whispering-gallery-mode lasing in liquid-crystal microdroplets," Opt. Express 19, 19836-19844 (2011).

[3] Humar, M. and Muševič, "3D microlasers from self-assembled cholesteric liquid-crystal microdroplets," Optics Express 18, 26995-27003 (2010).

[4] Peddireddy,K., Jampani, V. S. R., Thutupalli, S., Herminghaus, S., Bahr,Ch. and Muševič, I., "Lasing and waveguiding in smectic A liquid crystal optical fibers," Optics Express 21, 30233-30242 (2013).

[5] Peddireddy, K., Kumar, P., Thutupalli, S., Herminghaus, S. and Bahr, C., "Solubilization of Thermotropic Liquid Crystal Compounds in Aqueous Surfactant Solutions," Langmuir 28, 12426-12431 (2012).

[6] Smalyukh, I. I., Shiyanovskii, S. V. and Lavrentovich, O. D., "Three-dimensional imaging of orientational order by fluorescence confocal polarizing microscopy," Chem. Phys. Lett. 336, 88-96 (2001).

[7] Peddireddy, K., Kumar, P., Thutupalli, S., Herminghaus, S. and Bahr, C., "Myelin Structures Formed by Thermotropic Smectic Liquid Crystals," Langmuir 29, 15682-15688 (2013).

[8] Van Duong Ta, Rui Chen, Lin Ma, Yong Jun Ying, and, Han Dong Sun, "Whispering gallery mode microlasers and refractive index sensing based on single polymer fiber," Laser Photonics Rev. 7, 133–139 (2013).