the droplet is bipolar, as shown in the schematic drawing in Fig. 4(a). The observed WGM splitting suggests that the LC surface anchoring is not completely planar (i.e.with molecules parallel to the curved droplet interface), but slightly tilted, so that the boojums are not on the surface, but pushed outside the droplet. The two surface boojums are indeed rarely observed in the experiment (Fig. 4(b) and (c)). By increasing the SDS concentration to 0.2 mM, the bipolar configuration transforms into a single defect loop, encircling the microdroplet at the equator (the second panel in Fig. 4(a)). After increasing the SDS concentration to 0.3 mM, the ring becomes asymmetrically positioned, shrinking first into the radial hedgehog point defect (fourth panels in Fig. 4(a), (b) and (c)). This point defect, which is located at the surface of the microdroplet then sinks into the center of the microdroplet at 2 mM concentration of SDS. The director configurations in LC droplets at different SDS concentrations match the configurations reported in previous studies [11]. The changes induced by different surfactant concentrations are completely reversible, since the surfactant molecules on the interface are in thermodynamic equilibrium with the surrounding water solution [21] and can therefore adsorb and desorb from the surface.

We have measured the concentration dependence of the light emission from 5CB microdroplets in water solution. The corresponding changes in the WGM spectra are quite significant, as shown in Fig. 4(d) and (e). For bipolar and radial droplets we have proven lasing by measuring the threshold characteristics, but for intermediate droplet configurations, the spectral lines may not always be lasing. For the bipolar droplet configuration and the inner-ring configuration up to the SDS concentration of 0.2 mM, the spectra show characteristic bandstructure with a group of up to 10 lasing lines, separated by 0.5 nm. At the SDS concentration of ~ 0.2 mM, the band structure of the spectral lines starts to change. Some of the lines disappear and above 0.3 mM concentration, the lines previously forming a band, merge into a single line. The position of these merged lines shift strongly in the range of SDS concentration between 0.3 mM and 0.4 mM, and the spectrum looks quite chaotic. This chaotic spectrum changes when the droplet obtains the radial director configuration above 0.6 mM SDS concentration, and the spectra clearly shows stable lasing WGM lines, characteristic for the radial droplet structure. For the concentration range between $0.3 - 0.4$ mM, where the "chaotic" change in the spectral features occurs, a more detailed measurement was performed on a $16\,\mu$m droplet by changing the concentration in 0.02 mM steps (Fig. 4(e)). Wide lines are still observed in this range, however, they change the position and width in a quite unpredictable way, not following monotonically the increasing SDS concentration.

At this stage, it is not clear how to determine the exact concentration of SDS just by measuring the spectrum in this interval of chaotic spectra. However, the lasing spectrum is sensitive to a very small variation of SDS concentration, which could potentially lead to high sensitivity. On the other hand, we can clearly distinguish the situations, where the concentration of SDS is either bellow 0.2 mM or above 0.6 mM. We expect that this concentration "window" could be pushed to significantly lower values for some targeted molecules (of the order of one millionth), such as the endotoxins. It was recently demonstrated for endotoxins [13], that already very small concentrations can induce the change from bipolar to the radial configuration. Using our WGM lasing detection technique we could in this case determine the presence of toxins in the picogram per milliliter concentrations. The LC microdroplet sensors can be also used in non-lasing regime, that is below the lasing threshold. In this case, at low surfactant concentrations, no distinct spectral lines are present, but above SDS concentration of 0.5 mM, characteristic WGM lines appear serving as an indicator for the presence of the surfactant.

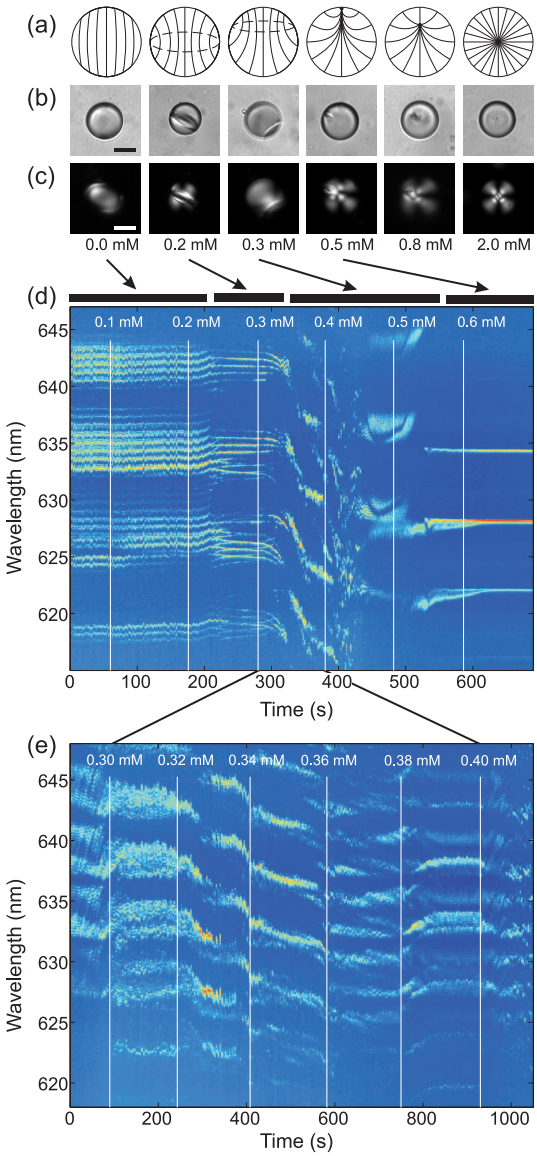

Fig. 4. Changes of the structure of a small droplet of the nematic liquid crystal at increasing concentrations of SDS. (a) The lines represent the orientation of the long axes of the LC molecules. The dots are point defects, where the orientation is not defined. In pure water, the LC molecules align parallel to the water-LC interface and the structure is bipolar. By increasing the SDS concentration, the surface anchoring of LC molecules gradually changes towards the perpendicular molecular orientation, obtained at 2.0 mM of SDS and beyond. (b) Non-polarized optical microscope images of $\sim 17\,\mu$m diameter microdroplets of 5CB in water and SDS. The "inner" ring is observable at 0.2 mM of SDS. The point defect evolves at the surface and sinks into the center at 0.8 mM concentration of SDS. Scale bar $10\,\mu$m. (c) The same images as in (b), taken between crossed polarizers. (d) The spectrum of laser light, emitted from a $13\,\mu$m 5CB droplet in water with various concentrations of SDS added. (e) Part of the lasing spectrum in the "chaotic" regime of intermediate SDS concentrations ($0.3-0.4$ mM) of a $16\,\mu$m droplet.

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5. Conclusion

Our results demonstrate that lasing from LC microdroplets provides for a versatile and simple method of monitoring the internal orientational structure of LC microdroplets. Because the orientation of LC inside the droplet critically depends on the anchoring of the LC at the surface of microdroplets, the lasing spectra provides direct information on the molecular adsorption/desorption processes at the surface of microdroplets. The developed sensing method could be easily integrated into existing microfluidics chips. Monodispersed LC droplets could be formed within a microchannel [22] and the excitation and detection of fluorescent light could be achieved through the integrated optical fibers [23]. Monitoring and automated recognition of the lasing spectra from LC microdroplets has therefore a clear advantage in comparison to the conventional observation of individual droplets under an optical microscope and could provide efficient and automated readout of the presence of targeted molecules in water, surrounding the LC microdroplet sensor.

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