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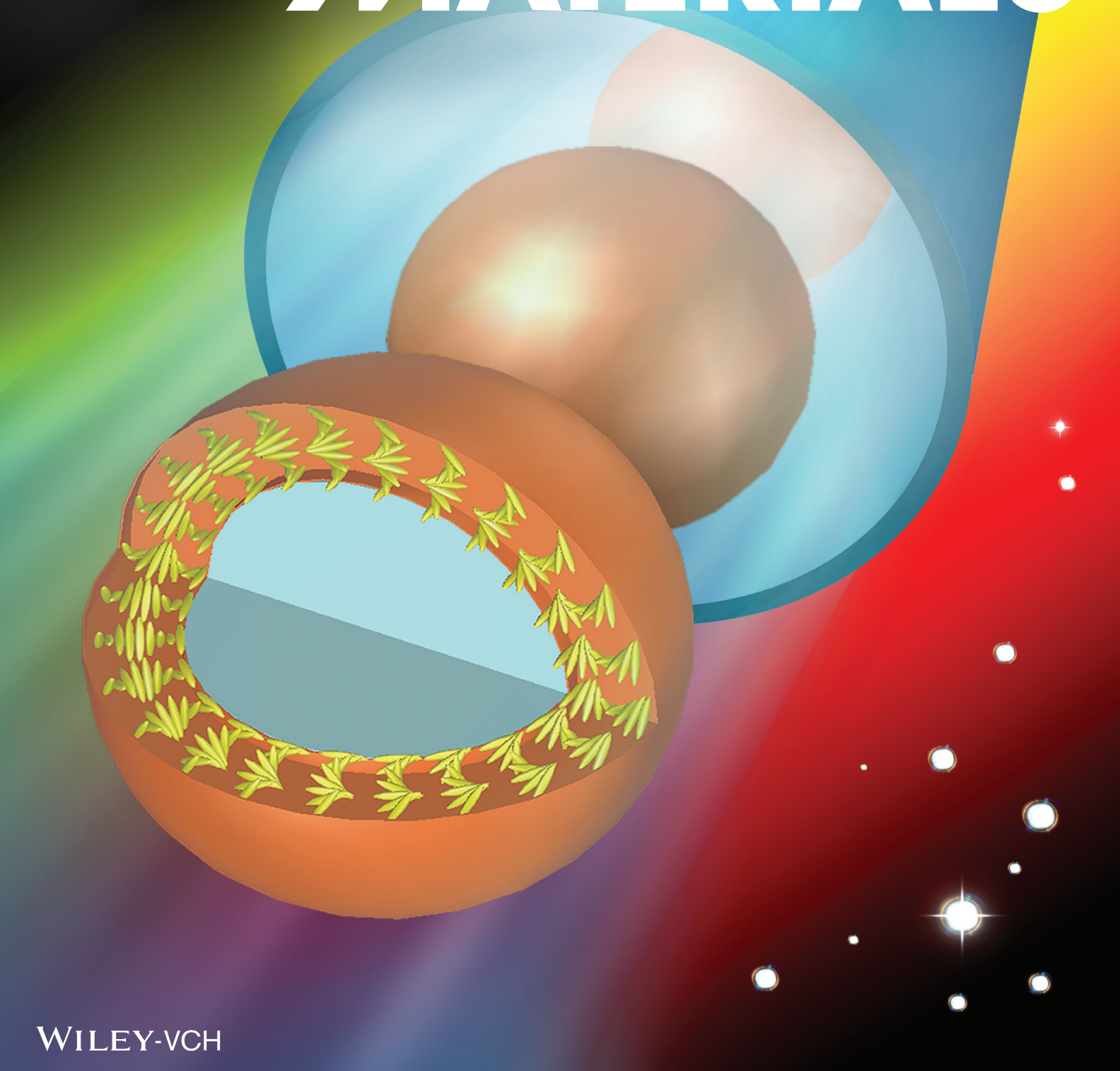

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Photoresponsive Monodisperse Cholesteric Liquid Crystalline Microshells for Tunable Omnidirectional Lasing Enabled by a Visible Light-Driven Chiral Molecular Switch

*Lujian Chen, Yannian Li, Jing Fan, Hari Krishna Bisoyi, David A. Weitz, and Quan Li**

Bottom-up fabrication of 3D photonic structures with unique optical properties is currently a burgeoning area of research. In this context, cholesteric liquid crystals (CLCs) hold great promise and opportunities in optics and photonics owing to their self-organized periodic dielectric helical structure.[1] Since the CLC medium is highly birefringent, the helical structure causes a periodic modulation of the refractive index, consequently establishing a 1D photonic bandgap (PBG) centered at $\lambda = nP$ where P is the helical pitch and n is the average refractive index. In this wavelength region, light cannot propagate but the helical superstructures can selectively reflect light. The pitch of CLCs is highly sensitive to external stimuli such as temperature, light, electric field, magnetic field, mechanical stress, and chemical conditions. Among them, light is particularly fascinating due to its advantage of remote, spatial, and temporal controllability in a wide range of ambient environments. Given the widespread applications of phototunable CLCs in tunable color reflectors and filters,[2,3] tunable liquid crystal (LC) lasers,[4] optically addressed flexible displays without patterned electronics,[5] and biomedical applications,[6] it would be highly beneficial to employ photoresponsive 1D CLCs for constructing 3D photonic structures. Thanks to the recent development of microfluidic methods, the fabrication of stable 3D spherical microshells of anisotropic fluids in general and CLCs in particular with controllable size and shell thickness has been made possible.[7]

When CLCs are doped with an organic fluorescent dye as the light harvester, they can function as photonic band edge lasers if one of the PBG edges overlaps the emission spectrum of the dye. Such dye-doped CLC lasers have attracted a great deal of interest as compact, low-threshold, versatile and tunable coherent light sources in the field of soft matter photonics.[8–10] Moreover, 3D photonic microstructures show promising potential to realize omnidirectional, narrow line-width and controllable emission, which may significantly broaden the applications of CLC band edge lasers.[11] However, 3D lasing involving CLCs has not been much explored,[10,11] and there is no report on lasing using photoresponsive cholesteric microshells. Recently, a microfluidics-based method has been reported to generate CLC spherical shells that can serve as 3D photonic crystals for omnidirectional laser emission owing to the radial arrangement of helical axes within the cholesteric shells.[12] However, the band edge laser emission only occurs at a fixed wavelength.

Here we report a straightforward approach to fabricate photoresponsive CLC spherical microshells composed of the new visible light-driven chiral molecular switch (*R*)-**1** (**Figure 1**) and the commercially available fluorescent dye and LC.[13] The resulting microshells are monodisperse and can generate LC lasers with phototunable output wavelength. The photoisomerization of the light-driven switch molecules enables us to shift the wavelength of the LC laser by optical pumping, and fully recover the laser wavelength by keeping the sample in the dark. To the best of our knowledge, this is the first report on photoresponsive liquid crystalline microshells. It is also the first demonstration of a phototunable LC laser in the form of spherical CLC microshells, which is based on an interesting "pumping-self-tuning" mechanism.

The new visible light-driven chiral molecular switch (*R*)-**1** was prepared by a facile synthesis, and its chemical structure was well-identified by ^{1}H and ^{13}C NMR spectroscopy, and high-resolution mass spectrometry (see Supporting Information). It was chemically and thermally stable, and showed optically tunable behavior in both organic solvent and LC media. The chiral switch (*R*)-**1** exhibited a very high helical twisting power of 198 μm^{-1} at the initial state in an achiral LC E7, which decreased to 175 μm^{-1} upon irradiation with 530 nm light. As expected, doping it in E7 even at a low concentration can induce an optically tunable helical superstructure. The PBG of the CLC with 5.0 wt% (*R*)-**1** initially appears in the visible light region with the central wavelength around 550 nm (Figure S4). Upon irradiation with 530 nm light, the PBG shows a red-shift; finally at the photostationary state (PSS), the central wavelength of the PBG moves to 630 nm. The phototuning of PBG is the underlying mechanism for the potential laser tunability of this cholesteric material as the absorption of the chiral dopant overlaps with the wavelength of the pumping laser. We also observed a slight red-shift of ca. 10 nm in the reflection when 0.5 wt%

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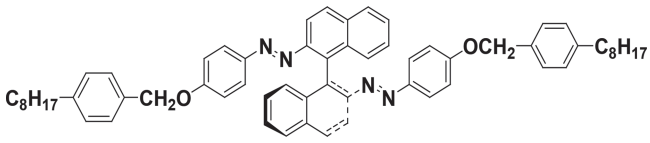

Figure 1. Chemical structure of a light-driven chiral molecular switch (*R*)-**1**.

of achiral 4-dicyanomethylene-2-methyl-6-(*p*-(dimethylamino) styryl)-4H-pyran (DCM) dye is added into this mixture (Figure S5). The phototuning range of the (*R*)-**1**/DCM/E7 mixture is from 560 nm to 640 nm.

To fabricate spherical CLC shells, we generated double emulsions using a glass capillary device with two tapered cylindrical capillaries coaxially assembled in a square capillary, as shown in **Figure 2**. Both the inner and outer phases are the aqueous solution of 10 wt% poly(vinyl alcohol) (PVA) (**Figure 3**). PVA macromolecules can help in stabilizing the double emulsion and impose parallel anchoring of the CLC molecules near the interfaces thus endowing radial orientation of the helical axes within the shells. The middle phase is a photoresponsive CLC composed of 4.7 wt% light-driven chiral molecular switch (*R*)-**1**, 94.8 wt% commercially available achial LC E7, and 0.5 wt% laser dye DCM. During the microfluidic fabrication, we heated up the middle phase using a syringe heater above the clear point of the CLC. This decreases the viscosity of the middle phase, and therefore allows a stable generation of double emulsion. By adjusting the flow rates of the three phases, we obtained monodisperse double emulsion drops, each containing a single drop in the core (see movie in Supporting Information).

When the flow rates for the inner, middle and outer fluids were 150 μL/h, 200 μL/h and 2000 μL/h respectively, we obtained monodisperse CLC microshells with a thickness of 18 μm as shown by both cross polarized and confocal microscopy images in **Figure 4** (also see Supporting Information Figure S3). We subsequently introduced the suspension of these CLC microshells in PVA solution into a 150-μm-thick glass cell by capillary force and sealed the cell with epoxy glue to avoid drying out and deformation of the structure. The microshells are quite stable upon thermal fluctuation even at the temperature higher than the clear point when no interference induced colorful pattern can be observed.

An inverted fluorescence microscope was used to observe the CLC microshells. We individually illuminated them by the second harmonic (532 nm) of a neodymium-yttrium-aluminum garnet (Nd:YAG) Q-switched laser (Quantel, Brilliant) operated at manual mode to release a pulse sequence with 5 ns duration and different time intervals. The pumping laser was focused on the center of the selected droplet through a 10× objective. The waist of the pumping laser beam is about 30 μm. The output from the samples was collected and detected by a QE65000 spectrometer (Ocean Optics, resolution 0.5 nm).

With a pulse energy of 10 μJ, we observed a single and sharp lasing peak centered at 596.6 nm in a 18-μm-thick microshell at the first shot, as shown in **Figure 5**A (also see Supporting Information Figure S5). The emission position of the laser from the CLC shell is comparable to the long wavelength edge of the reflection spectra, indicating a typical band-edge lasing. Since the laser emission occurs along the helix axis in cholesteric lasers, the microshell is capable of exhibiting lasing in all directions due to radial organization of helical axes imposed by the aqueous interfaces. The line width of the single-mode lasing is typically about 1.3 nm, which is also comparable to the width that we could obtain in thin planar CLC glass cells. The pumping light not only excited the laser dye, but also concomitantly tuned the laser wavelength owing to the overlap of its wavelength with the absorption of the chiral molecular switch. Thus, upon repeated pumping, a red shift in the lasing peak wavelength was induced due to the photoisomerization of the switch molecules and the consequent shift in PBG of the cholesteric microshell. By varying the flow rates of the three phases, we obtained different size drops. We investigated their emission behavior and found that only the microshells with thickness larger than 10 μm could emit laser light.

We further investigated the dependence of the laser output wavelength on the pumping pulse number for two pumping energies (5 μJ and 10 μJ) and two time intervals (5 s and 10 s). As shown in Figure 5B, although different pumping pulses were required, the peak wavelength always shifted from ~590 to ~640 nm, indicating that the tuning range is irrespective of

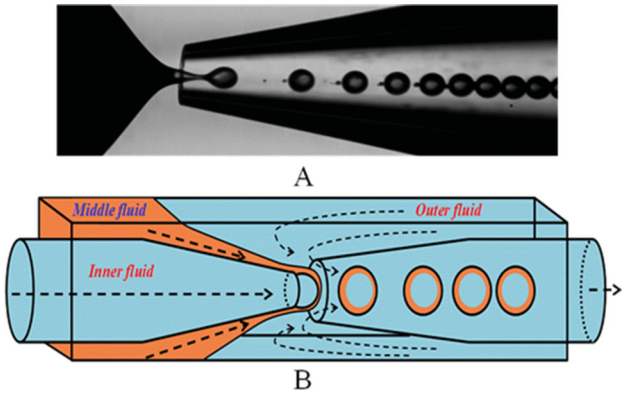

Figure 2. Micrograph (A) and schematic description (B) of the generation of photoresponsive monodisperse CLC microshells (water-in-oil-in-water double-emulsion drops) using a glass capillary microfluidic device. Note: inner and outer fluids (light blue) are the same aqueous solution, and the middle fluid (orange) is the photoresponsive CLC.

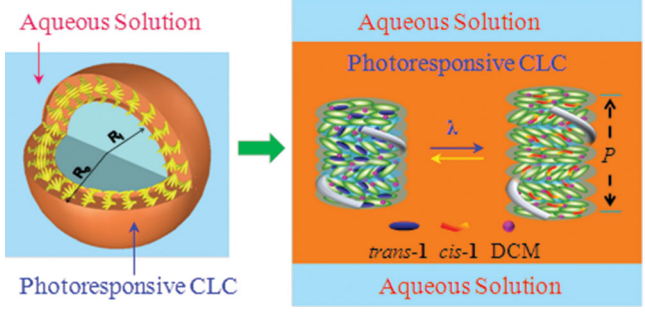

Figure 3. Schematic structure of the photoresponsive monodisperse CLC microshell as a water/oil/water double emulsion (left) and schematic mechanism of phototunable lasing enabled by a light-driven chiral molecular switch (*R*)-**1** (right). Note: inner and outer aqueous PVA solutions enforce the CLC molecules in a planar aligned state.

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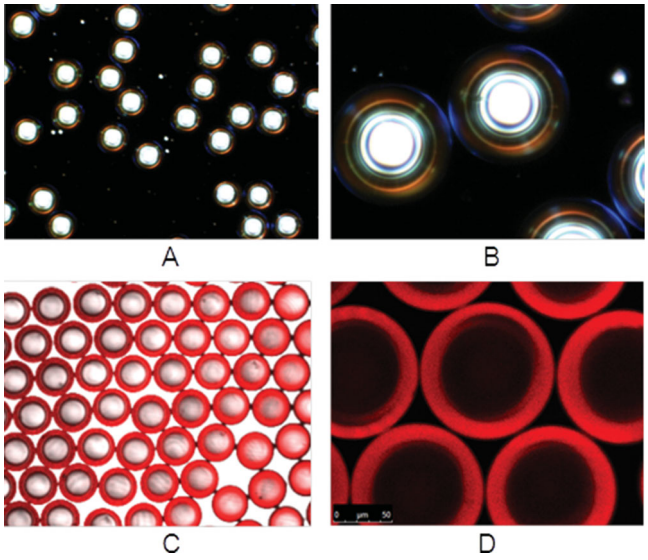

Figure 4. Crossed polarized (A,B) and confocal (C,D) images of the CLC shells with R_o = 58 μm and R_i = 40 μm taken under microscope with different magnification.

the pumping energy or time interval. The comparable tuning range in these cases might result from the same PSS of the chiral molecular switch molecules, which only depends on the pumping light wavelength.[14] In all cases, the total pumping

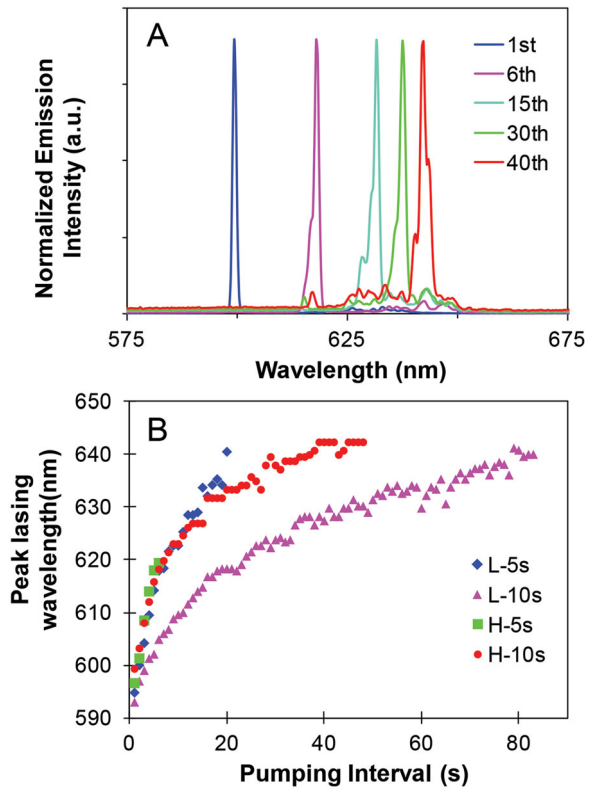

Figure 5. A: Variation of laser emission of (*R*)-**1**/DCM/E7 CLC shells after pumping different times of 532 nm light at pumping energy of 10 μJ with 10 s time interval. B: Shift of band-edge lasing peak after different pumping intervals with different pumping energy (L: 5 μJ and H: 10 μJ).

pulse number required for the peak lasing wavelength shifting from 590 to 640 nm varies with the pulse energy of the irradiation source. When irradiated by a 5 μJ laser source at 10 s time interval, the CLC shells reached the PSS after about 80 pulses. The band-edge lasing line fully recovered to its initial wavelength position after being placed in darkness for 12 h.

Higher laser source energy or smaller time interval led to faster tuning speed (steeper slope). If the pumping time interval is small enough or the pumping energy is high enough, only the first emission of the band-edge lasing could be observed. This phenomenon could be explained by the interplay between the absorption-induced red shift of the PBG and the diffusion of unaffected CLC molecules into the affected region. The *cis-trans* back-relaxation is not quick enough and hence not favored in such a short time interval when the light is off. So the diffusion process of the *trans*- and *cis*-form of the chiral switch in different regions should be taken into consideration. We are currently working on developing the thermodynamics model to describe the process.

In conclusion, we have, for the first time, demonstrated the fabrication of photoresponsive monodisperse CLC microshells using a glass capillary microfluidic device. The photoresponsive CLCs have been formulated by doping a novel visible light-driven chiral molecular switch into the commercially available LC E7. In the presence of DCM dye, these microshells exhibited photonic band edge laser emission in all directions due to the radial disposition of the CLC helices within the shells. The laser emission wavelength self-tunes from ~590 to ~640 nm when pumped due to the simultaneous photoisomerization of the chiral molecular switch. After storage in darkness for 12 h, the emitting wavelength fully recovered to its initial state. This new organic soft and dynamic photonic band gap structures may be useful for biological imaging and sensing in addition to 3D photonic band gap applications. This study has opened up some interesting possibilities. For example, appropriate combination of materials by judicious choice may lead to phototunable lasing across the full visible range, thus providing omnidirectional red, green and blue lasers from the same microshell. The concept disclosed and demonstrated here could also be extended to study the effect of light-driven in-situ helix inversion on lasing in such photoresponsive cholesteric microshells and beyond.

Experimental Section

All chemicals and solvents were purchased from commercial supplies and used without further purification. Poly(vinyl alcohol) (PVA) is purchased from Sigma-Aldrich (MW: 13 000–23 000 g/mol, 87–89% hydrolyzed). The commercially available achiral nematic LC E7 was used in the study, which is a eutectic mixture of LC components commercially designed for display application. The fluorescent dye 4-dicyanomethylene-2-methyl-6-(*p*-(dimethylamino)styryl)-4H-pyran (DCM) is obtained from Exciton and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$. ^{1}H NMR (400 MHz) spectra were recorded on a Bruker 400 spectrometer and ^{13}C NMR (50 MHz) spectra were recorded on a Varian 200 spectrometer. Chemical shifts are in δ units (ppm) with the residual solvent peak or TMS as the internal standard. The coupling constant (J) is reported in hertz (Hz). NMR splitting patterns are designated as follows: s, singlet; d, doublet;

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t, triplet; and m, multiplet. Column chromatography was carried out on silica gel (230–400 mesh). Analytical thin layer chromatography (TLC) was performed on commercially coated 60 mesh F_{254} glass plates. Spots were rendered visible by exposing the plate to UV light. Textures and disclination line distance changes were observed by optical microscopy using a Leitz or Nikon polarizing microscope. UV-vis spectra were measured by a Perkin Elmer Lambda 25 Spectrometer. The UV and visible light irradiation was carried out Xenon light source 100 W through a filter at 310 nm or 550 nm. Reflection spectra were examined with an Ocean Optics spectrometer collecting spectra in the dark. Round glass capillary tubes (World Precision Instruments) with outer and inner diameters of 1.00 mm and 580 μm, respectively, were tapered to the desired diameter using a micropipette puller (Sutter Instrument, P-97) and a microforge (Narishige, MF-830). The diameters of typical orifices of the capillaries for inner fluid and for collection were 20–50 μm and 50–200 μm, respectively. The round tapered capillaries for inner phases and collection were treated with a hydrophobic reagent (trimethoxy(octadecyl)silane, Sigma-Aldrich Co.) and a hydrophilic reagent {2-[methoxy(polyethyleneoxy)-propyl]-9–12 trimethoxysilane, Gelest, Inc.}, respectively. The round capillaries were then fitted into a square capillary (Atlantic International Technology), which has an inner dimension of 1.05 mm. The distance between the two round capillaries for inner fluid and collection was adjusted to be 30–150 μm. All the fluids were pumped into the capillary microfluidic device using syringe pumps (Harvard PHD 2000 series). A typical set of flow rates for the inner, middle, and outer phases were 150, 200, and 2000 μL/h, respectively. Triggered nanosecond laser pulses of 532 nm from a Nd:YAG Q-switched laser (Quantel, Brilliant) was guided into an Olympus IX70 inverted fluorescence microscope to irriadiate the CLC microshells in a epi-illumination manner. A Thorlabs DCC1545M CMOS camera was used to observe and locate the individual microshell. An Ocean Optics QE65000 spectrometer attached to the inverted microscope was used to collect the omnidirectional laser spectra.

Supporting Information

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

Acknowledgements

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