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Optically generated adaptive localized structures in confined chiral liquid crystals doped with fullerene

O. Trushkevych,[1,2] P. Ackerman,[1] W. A. Crossland,[2] and I. I. Smalyukh[1,3,a)]
[1]*Department of Physics and Liquid Crystal Materials Research Center, University of Colorado, Boulder, Colorado 80309, USA*
[2]*Department of Engineering, University of Cambridge, Cambridge CB3 0FA, United Kingdom*
[3]*Renewable and Sustainable Energy Institute, University of Colorado, Boulder, Colorado 80309, USA*

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We report the facile optical creation of switchable localized structures in chiral liquid crystals doped with fullerene. In a cholesteric cell unwound by vertical boundary conditions, the initially dispersed fullerenes are deposited from the bulk to the surface of confining glass plates by low-intensity illumination. This alters the surface boundary conditions and allows for the creation of localized particlelike structures with twist-bound defects (dubbed Torons) that are controlled by electric fields and arranged into patterns of interest for photonic and electro-optic applications. © *2010 American Institute of Physics*. [doi:10.1063/1.3518477]

Control of structural organization in liquid crystals (LCs) using light and fields and, in turn, control of light by LCs are fascinating research themes that strongly influence technologies and consumer devices.[1] Cholesteric LCs are interesting from this standpoint due to the multitude of ground-state and metastable twisted structures as well as because of the unprecedented richness of light-matter interactions that they offer.[2] Their twisted ground-state structure is characterized by pitch p, the distance over which the director $\mathbf{n}(\mathbf{r})$ rotates by 360°. When this LC is introduced into a thin cell of thickness $d<p$ with vertical (homeotropic) surface anchoring of $\mathbf{n}(\mathbf{r})$, the incompatibility of these boundary conditions with the cholesteric helix results in structural frustration and tends to unwind the helicoidal structure. Although $\mathbf{n}(\mathbf{r})$ is typically untwisted for $d/p<1$, a number of locally twisted metastable and stable structures occur spontaneously[3,4] and can be generated by the use of external fields.[1–4] Various localized structures called "Torons" can be generated using laser beams with optical phase singularities[2] that reorient $\mathbf{n}(\mathbf{r})$ to transform the initially unwound structure to a twisted configuration with point or line singularities. On the other hand, LCs doped with dyes and nanoparticles, such as fullerene (C_{60}), exhibit enhanced optical realignment effects, which may have bulk or surface origin (due to dye or fullerene segregation to surfaces in the later case).[5–11]

We report the optical creation of Torons via a prolonged local low-intensity illumination that deposits fullerene from the bulk dispersion to the surface.[10,11] This process changes surface boundary conditions for $\mathbf{n}(\mathbf{r})$ from vertical to tangential or tilted, inducing twist and Torons in an initially unwound fullerene-doped LC. The Torons are controlled by electric fields and arranged into periodic arrays or arbitrary patterns that may be used as tunable photonic or diffractive elements.

Cholesterics of desired pitch p are prepared using a nematic host 5CB doped with a chiral agent CB15 (EM Industries, USA) of concentration $C_{\text{agent}}=1/(H_{\text{HTP}}\cdot p)$, where H_{HTP} is the helical twisting power measured using the Grandjean–Cano method.[4] The LCs are doped with 0.01–0.1 wt % of C_{60}. No phase separation is observed at these concentrations. Cholesterics are confined between glass plates with transparent conductive indium tin oxide coatings treated with DMOAP (N,N-dimethyl-n-octadecyl-3-aminopropyltrimethoxysilyl chloride) or Teflon for vertical alignment. The cell gap d is specified by spacers and set to $d\approx 0.8p \approx 11$ μm. For fluorescence confocal polarizing microscopy (FCPM),[2] the LCs are doped with ~0.01 wt % of dye n,n'-bis(2,5-di-*tert*-butylphenyl)-3,4,9,10-perylene dicarboximide.

Since C_{60}-doped samples show no detectable absorption at 1064 nm but strongly absorb at 488 nm, we use both blue and infrared light to induce Torons. Illumination at 488 nm is performed using an Ar laser and scanned mirrors of a confocal microscope (FV-300, Olympus, Olympus, Japan), while the spatial patterning of the focused 1064 nm beam (ytterbium-doped fiber laser) is achieved using a holographic optical tweezer (HOT) setup.[2] Both confocal and HOT systems are integrated with the same inverted microscope (IX-81, Olympus).[2] Laser power is continuously varied within 0.001–50 mW in the sample. The generating beam is focused into a submicron area using an oil-immersion objective (60×, NA=1.4). Electric fields are applied using a function generator DS340 (Stanford Research Systems, Olympus, Japan).

Focused Ar laser beam causes slow irreversible deposition of C_{60} from the bulk dispersion to the surface, modifying the boundary conditions for $\mathbf{n}(\mathbf{r})$ in a region of about 1–2 μm in diameter (Fig. 1). For a beam focused in the cell midplane, about equal C_{60} deposit areas on both surfaces result in distorted near-surface regions visualized by FCPM [Fig. 1(c)]. After sufficiently long illumination (15–60 s), a Toron spontaneously appears in the initially unwound LC and is long-term stable after illumination stops. Torons can be generated at desired locations and arranged into arbitrary patterns (Fig. 2). Their size can be electrically controlled, leaving only weak local distortions of $\mathbf{n}(\mathbf{r})$ and the fullerene deposit at high U [Figs. 2(b), 2(e), and 2(h)]. Once U is turned off, the Torons reappear for the deposits larger than ~1 μm in diameter but not for the smaller ones (Fig. 2).

[a)]Electronic mail: ivan.smalyukh@colorado.edu.

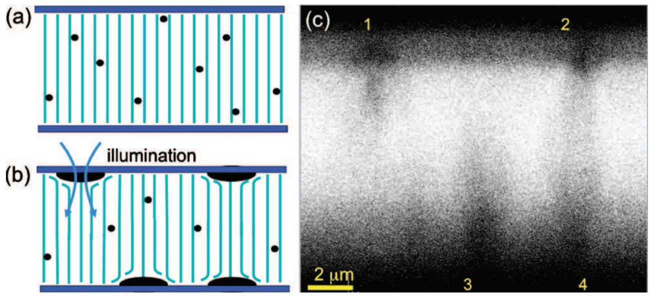

FIG. 1. (Color online) Fullerene deposition from the bulk dispersion onto substrates via illumination at 488 nm. [(a) and b)] **n**(**r**) in an unwound cholesteric cell doped with C_{60} (a) before and (b) after the illumination. (c) FCPM vertical cross section shows deposition of C_{60} upon illumination for 30 s with the light focused at the top surface (marked 1), bottom surface (3), and in the cell midplane (2 and 4). Areas around deposits are dark due to optical absorption and fluorescence quenching caused by C_{60}.

Stable Torons are also induced using a 1064 nm laser beam in a process similar to what we reported previously;[2] the required powers are typically higher than for blue light (≳10 mW) but still three to five times smaller than for undoped samples (~50 mW). The decrease of the threshold laser power needed to induce the T3-1s with a 1064 nm beam is due to the enhancement of the optical reorientation of **n**(**r**) enabled by fullerene doping, similar to that in dye-doped LCs.[12,13] However, these Torons do not reappear after turning off U, in contrast to the ones generated by blue light [Figs. 2(d)–2(i)] because, due to the low absorption, infrared beam does not deposit fullerene.

To get insights into the internal structure of Torons, we have studied **n**(**r**) in lateral and vertical cross sections similar to the ones shown in Figs. 3(a) and 3(b). The structures generated by infrared laser light are the regular triple twisted Torons, T3-1s, composed of a looped double twist cylinder (i.e., a loop of twist-escaped "+1" disclination) and accompanying hyperbolic bulk point defects bound by the twist [Fig. 3(d)].[2] However, the Torons induced via the optical deposition of fullerene, while also possessing the looped double twist cylinder, have point defects (boojums) located at the cell substrates in the place of the fullerene deposit and will be referred to as $T3_{sfd}$-1, with "sfd" indicating the surface fullerene deposit location of the defects. For certain fullerene deposits, we have also observed half-integer surface disclination rings replacing the boojums on one ($T3_{sfd}$-2) or both sides ($T3_{sfd}$-3) of the Toron structure shown in Fig. 3(e), which resembles the regular Torons of T3-2 and T3-3 types having similar defect loops but in the LC bulk rather than at surfaces.[2]

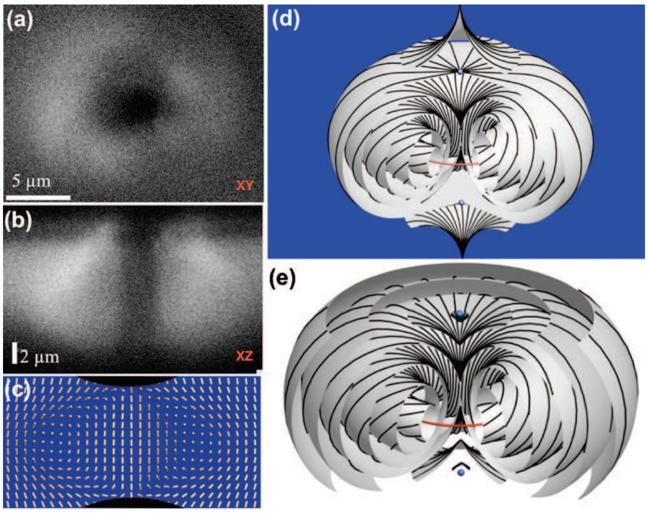

FIG. 3. (Color online) FCPM imaging and **n**(**r**) of Torons. [(a) and (b)] Confocal images in the lateral and vertical planes of the $T3_{sfd}$-1. (c) Reconstructed **n**(**r**) of the $T3_{sfd}$-1 in the vertical cross section corresponding to the image shown in (b). [(d) and (e)] Reconstructed **n**(**r**) for the T3-1 and $T3_{sfd}$-1 structures.

The lateral size of Torons is comparable to p (Fig. 4). $T3_{sfd}$-1 s with the surface-bound boojums are 1.2–1.45 times larger than T3-1s with bulk point defects. $T3_{sfd}$-1 and T3-1 shrink with increasing U because of the LC's positive dielectric anisotropy. T3-1 disappears at a certain U (showing discontinuous voltage dependence of its size), while $T3_{sfd}$-1 uniformly shrinks in size until it becomes comparable to the size of the fullerene deposit. Switching behavior can be controlled by tuning the deposit size as shown in Figs. 2(a)–2(c): after turning U off, the $T3_{sfd}$-1 reappears only in two preselected locations of the array that have larger C_{60} deposits.

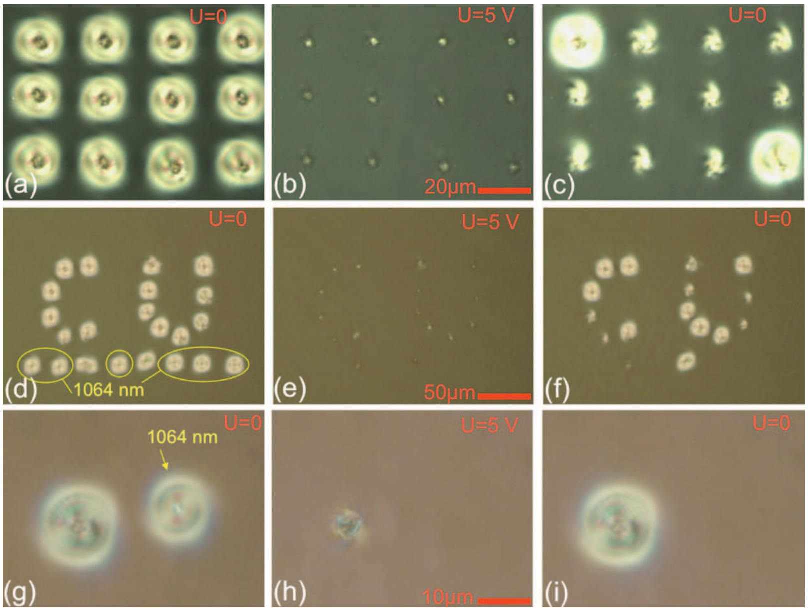

FIG. 2. (Color online) Laser-induced patterns of T3-1s and $T3_{sfd}$-1s. [(a)–(c)] An array of $T3_{sfd}$-1s induced via the illumination at 488 nm that deposits C_{60}. [(b) and (c)] The $T3_{sfd}$-1s can be designed (c) to fully reappear or not after turning off U (c). [(d)–f)] Voltage-controlled pattern containing $T3_{sfd}$-1s induced by 488 nm illumination and T3-1s induced by a 1064 nm laser. [(g)–(i)] T3-1 and $T3_{sfd}$-1 Torons induced next to each other: the T3-1 induced at 1064 nm (right) has no detectable deposit of fullerene on the surface and [(h) and (i)] does not reappear (h) after application and (i) turning off U.

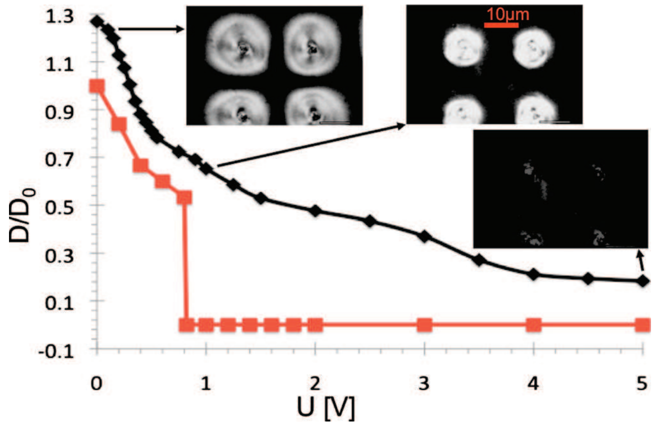

FIG. 4. (Color online) Voltage dependence of the size D of $T3_{sfd}$-1s (diamonds) and T3-1s (squares) normalized by the size D_0 of a T3-1 at $U=0$ measured using images (insets).

Nucleation of $T3_{sfd}$-1s is driven by the surface anchoring transition due to deposition of fullerene and corresponding surface anchoring free energy $F_s \sim WL^2$, where $W \sim 10^{-5}$ J/m^2 is the typical polar anchoring coefficient and $L \sim 10^{-6}$ m is the lateral size of the deposit. Placing two point defects at the surface rather than in the bulk also reduces the defect core energy by $F_c \sim 4\pi r_c^3 \varepsilon_c/3$ (thus, reducing the free energy barrier between the twisted and untwisted states), where r_c is the core radius of the point defect and ε_c is the LC's melting free energy density. However, for typical $\varepsilon_c \sim 10^5$ J/m^3 and $r_c \sim 10$ nm, F_c is much smaller than F_s, and thus, the transition is driven mostly by the change of F_s. The illumination of the LC deposits thin fullerene patches and nucleates Torons at low laser powers ~10 μW. Since the energy barriers between locally twisted and untwisted states are $\gg k_B T$, external electric or optical fields are needed to push the system over this barrier so that the induced structures are stable over long time. Low-power approaches of recording Torons may allow simultaneous generation of arbitrary large arrays of these localized structures useful for applications in adaptive photonic and diffractive devices. LC displays may be engineered by using fullerene deposits to direct the initial alignment and switching of various twisted $\mathbf{n}(\mathbf{r})$ configurations, similar to the use of protrusions and patterned electrodes in vertical alignment displays.[1]

In conclusion, we have demonstrated the optical generation of adaptive localized structures in chiral nematics doped with fullerene via prolonged illumination with focused low-intensity light. These tunable structures of Torons have surface point defects or surface disclination loops colocated with the fullerene deposits. Similar generation of Torons may be achieved by using other dopants, such as dyes and colloidal nano- and micro-sized inclusions.[14–17] Periodic and arbitrary patterns of electrically tunable Torons, with sizes varying from ~100 nm to hundreds of micrometers, can be achieved and used in photonic, diffractive, and electro-optic applications.

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