

Responsive, 3D Electronics Enabled by Liquid Crystal Elastomer Substrates

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Experimental details:

LCE substrates preparation: To prepare programmed molecular alignment in LCE substrates, a previously described photoalignment method was adopted to create patterned surfaces on the glass substrates.^{1,2} Briefly, 1 wt. % of a photoalignable dye, brilliant yellow (Sigma Aldrich), was dissolved in dimethylformamide (DMF, Fisher Scientific) then filtered by a 0.45 μm filter (Whatman). Then, glass substrates (75 mm $\times$ 51 mm $\times$ 1.2 mm, Electron Microscopy Sciences) were cleaned by sonication for 5 min each in laboratory detergent Alconox (Alconox Incorporation), acetone, and isopropanol, and DI water and subsequently dried with nitrogen. The cleaned glass slides were treated with oxygen plasma (Sirius T2, Trion Technology) for 1 minute at 100 mTorr pressure and 50 mW power. The prepared brilliant yellow solution was then spin-coated onto the cleaned slides at 750 rpm (1500 rpm/sec) for 10 seconds and at 1500 rpm (1500 rpm/sec) for 30 seconds. The brilliant yellow-coated glass substrates were exposed to linearly polarized broadband light at an intensity of 10 mW/cm² (Vivitek D912HD) for 2 min. A pair of programmed glass slides were assembled 37.5 μm apart using a spacer (Precision Brand) along the edges. To prepare LCE substrates in the photopatterned glass cell, a liquid crystal monomer, 1,4-bis-[4-(6-acryloyloxyhexyloxy)-benzoyloxy]-2-methylbenzene (RM82, Wilshire Chemicals), a chain extender molecule, n-butylamine (Sigma Aldrich), and a photoinitiator, Irgacure I-369 (BASF) were used as described in previous publications.^{1,2} The RM82 and n-butylamine with a molar ratio of 1.1:1 (diacrylate:amine) were mixed with 1.5 wt. % of the photoinitiator. The mixture was heated and vortexed then filled into the photopatterned cell by capillary action. The cell was kept at 65 °C oven for 15 hours for oligomerization. Then, the oligomerized samples were exposed to 250 mW/cm² intensity of 365 nm UV light (OmniCure® LX400+, Lumen Dynamics) for 5 min for crosslinking. After crosslinking, the top-side glass slide was gently removed. A

polarizing optical microscope (POM) (Olympus, BX51) was used for optical characterization of alignment. A dynamic mechanical analyzer (DMA) (TA Instruments, RSA-G2) was used to test the thermomechanical properties of LCE substrates. Planar aligned LCE films were cut either along or perpendicular to the director with a dimension of 10 mm $\times$ 2 mm $\times$ 37.5 μ m. Three samples were tested for each configuration. To measure actuation strain, samples were heated and cooled three times from 150 to -75 $^{\circ}$ C at a rate of 5 $^{\circ}$ C/min while holding a load of 0 N.

3D pop-up LCE conducting traces: To fabricate micro-scale conducting traces on the programmed LCE substrates, 5 nm of chromium and 200 nm of gold were serially deposited via e-beam evaporation (Temescal BJD-1800). The deposition rate was set to 1-2 $\text{\AA}$ /sec. After deposition of the Cr/Au layers on the LCE substrates, a positive photoresist (Shipley S1805) was spin-coated at 2000 rpm (3000 rpm/sec) for 60 seconds and baked at 85 $^{\circ}$ C for 12 min. To develop the coated photoresist layer, a Karl Suss MA6 Mask Aligner was used with 75 mJ/cm² of UV light exposure with a patterned mask. After exposure, samples were immersed in Microposit MF-319 (Dow Chemical, USA) for 60 sec, then rinsed with DI water. Then Au and Cr layers were patterned by soaking in a gold etchant (Transene Company) for 30 sec and chromium etchant (KMG Electronic Chemicals) for 10 sec, respectively. The remaining photoresist was removed by flood-UV exposure and subsequent immersion in MF-319. To finalize the process, micro-scale conducting traces patterned LCEs were coated by 800 nm hard mask of silicon nitride at 150 $^{\circ}$ C using Plasma Enhanced Chemical Vapor Deposition (Mykrolis Corporation, Unaxis 790 PECVD). Adhesion layer of hexamethyldisilazane (HMDS) was vapor-deposited at 120 $^{\circ}$ C onto the silicon nitride. Then a positive photoresist (Shipley S1813) was spun with 500 rpm (100 rpm/sec) for 10 sec and 200 rpm (300 rpm/sec) for 60 sec. After coating of photoresist, samples were soft baked at 85 $^{\circ}$ C

for 12 min and exposed to 150 mJ/cm^2 of UV light (Karl Suss MA6 Mask Aligner) through a mask that defines the outer edges of the device. The exposed samples were immersed into Microposit MF-319 (Dow Chemical, USA) for 60 sec, then rinsed with DI water. The hard mask layer, silicon nitride, was patterned using dry etching by 120 mTorr pressure and 100 W power with SF₆ saturated environment (Sirius T2, Trion Technology) for 15 min. The LCE was then etched by 220 mTorr pressure and 200 W power with oxygen plasma for 90 min. After dry etching processes, the remaining silicon nitride was removed by immersion into hydrofluoric acid (1:10) (HF) for 60 sec. Micro-scale conducting traces were then released from glass slides by soaking in a 15 wt. % potassium borate solution (AZ400K, AZ Electronic Materials) for 30 min. Finally, released devices were gently washed by DI water and subsequently dried with nitrogen. The resistance of each device was measured by electrical multimeter (Fluke 114). A total of 9 electrodes (3 electrodes from 3 devices) were measured for each type of device. For mechanical stress-strain test, devices were stretched with constant linear rate of 0.1 mm/sec using the DMA described previously.

3D pop-up LCE-MIM-Cap: Fabrication of MIM capacitors was carried out using standard cleanroom microfabrication techniques. First, a surface-aligned LCE film was prepared on a glass slide as aforementioned. A bottom metal layer of Cr/Au (10/190 nm) was deposited using an AJA ATC Orion magnetron sputtering system and patterned by a standard wet etch process as mentioned in the previous section. A Parylene-C layer (300 nm) was deposited as capacitor dielectric using a Specialty Coating Systems PDS 2010 Labcoater 2. Parylene-C was patterned by reactive ion etching (RIE) in an oxygen plasma. A top metal layer of Ti/Au (10/190 nm) was deposited and patterned similarly as the top metal layer. Finally, device definition was performed

by manually cutting device boundaries with a razor blade and soaking the sample in 15 wt. % potassium borate solution for 30 min to release the LCE-MIM-Cap from the glass slide. Electrical characterization of MIM capacitors was carried out using a Keithley 4200 Semiconductor Characterization System. Capacitance-frequency measurements were performed over a frequency range from 10 kHz to 1 MHz under a voltage bias of 1 V. Three samples were measured. Capacitance-voltage measurements were performed under voltage biases from -5 to +5 V at 1 MHz.

3D reconfigurable LCE antennas: Fabrication of LCE antennas can be carried out e-beam evaporation (Temescal BJD-1800) of 200 nm gold on room temperature crosslinked twisted nematic LCE substrates. The deposition rate was set to 1-2 Å/sec. 12.5 µm spacers were used for the antenna. The LCE antenna dimensions are 30 mm × 2 mm × 12.7 µm. The aspect ratio (i.e., length/width) of the LCE strips had to be large enough (>10) to achieve the needed shape transformations, such as, helices or spirals. The aspect ratio for our film is 15. The LCE antenna was used as a sensor by relating the change of its shape to a detectable change in its electrical properties. Large flask of cooling bath was filled with dry ice and isopropyl alcohol (IPA); creating a temperature of -75 °C. A thermocouple was used to monitor the uniform temperature and additional fresh dry ice was added to the bath periodically, to maintain a constant temperature of -75 °C. The two probe resistance measurements were performed using Keithley 4200-SCS to obtain an I-V curve with a voltage sweep from -1V to 1V and a sweep step of 0.01V. The resistance is calculated as the gradient (change in voltage divided by change in current) of the I-V curve. All samples were 5mm by 2mm, measured at room temperature in ambient air and probed at the same

distance. The 5 mm by 2 mm Au film resistance measurements after 50 cold cycles was 4.4Ω . Detailed theory-based antenna analysis is described in later part of this supporting information.

Supporting Figures:

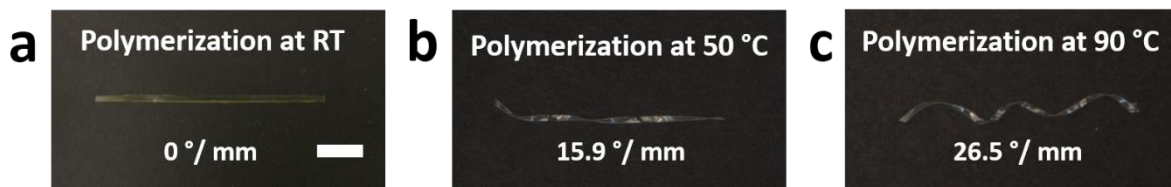


Figure S1. LCE shapes controlled by polymerization at room temperature (a), 50 °C (b), and 90 °C (c). (Scale bar = 1 cm)

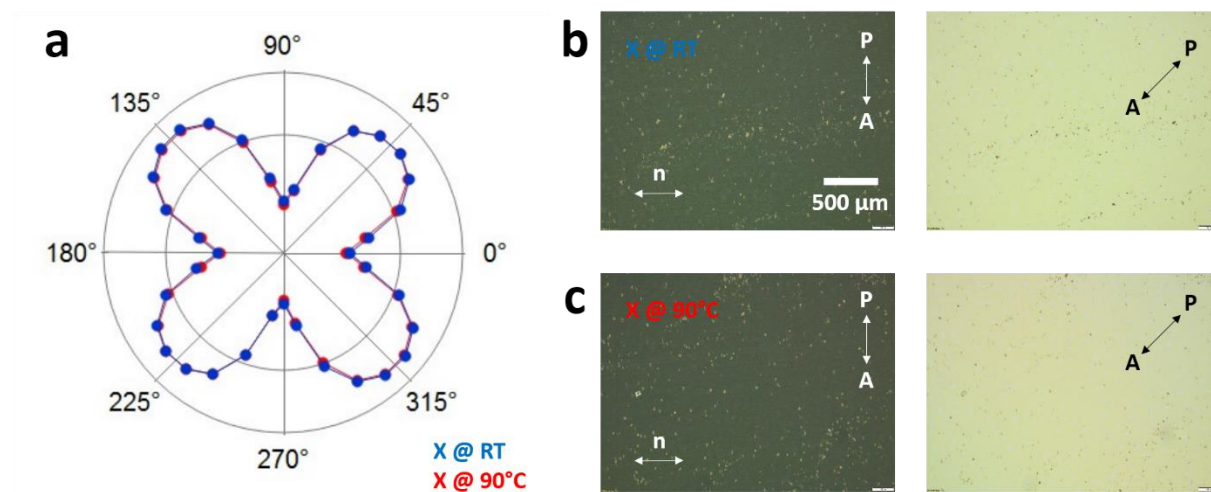


Figure S2. (a) Transmission of light through an RT-LCE and HT-LCE between parallel polarizers in the room-temperature twisted nematic state. Birefringence of RT-LCE (b) and HT-LCE (c).

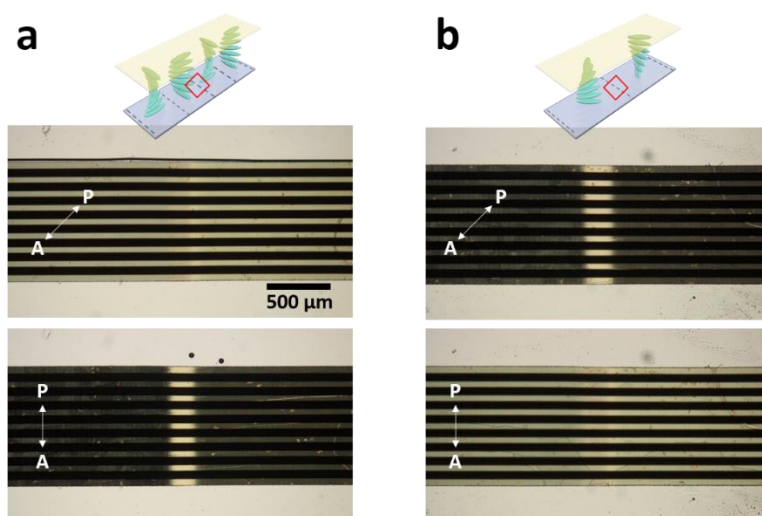


Figure S3. Schematic and characteristic birefringence optical properties of wavy (a) and helical inversion (b) LCE with conducting traces, respectively. Red boxes indicate LCE molecular patterning boundaries of each device.

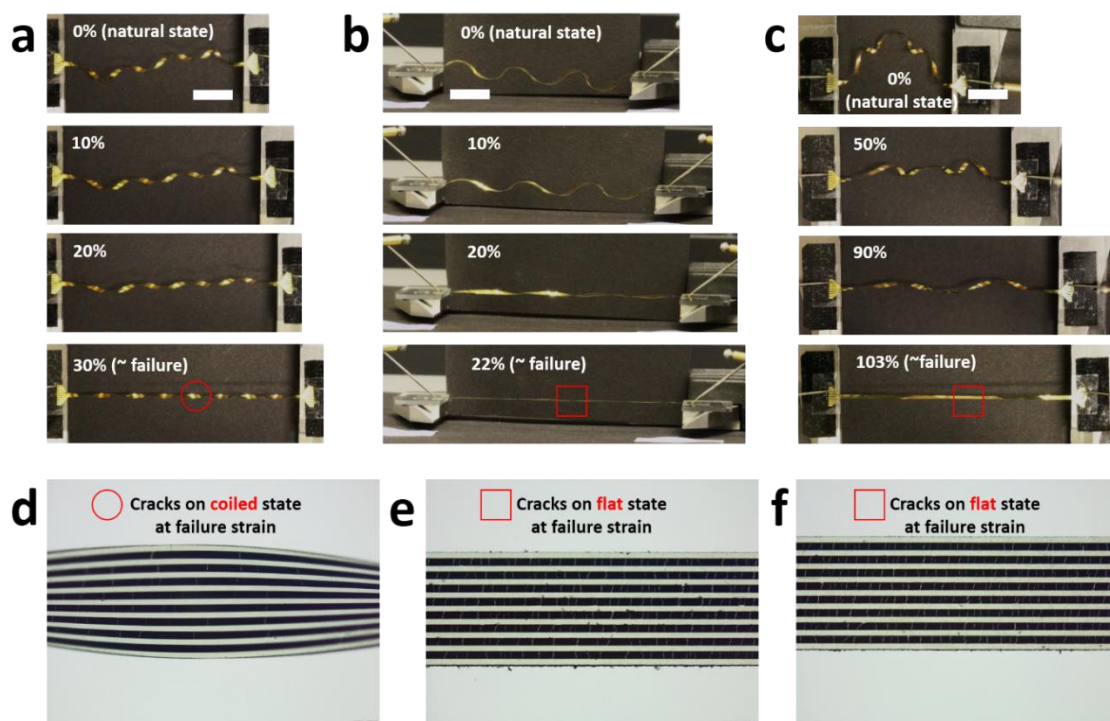


Figure S4. Macroscopic deformation during stretching of helical (a), wavy (b), and helical inversion (c) LCEs with conducting traces. Transmission optical micrographs of helical (d), wavy (e), and helical inversion (f) LCEs with conducting traces. Red circle and boxes indicate location of microscope images. (Scale bar = 1 cm)

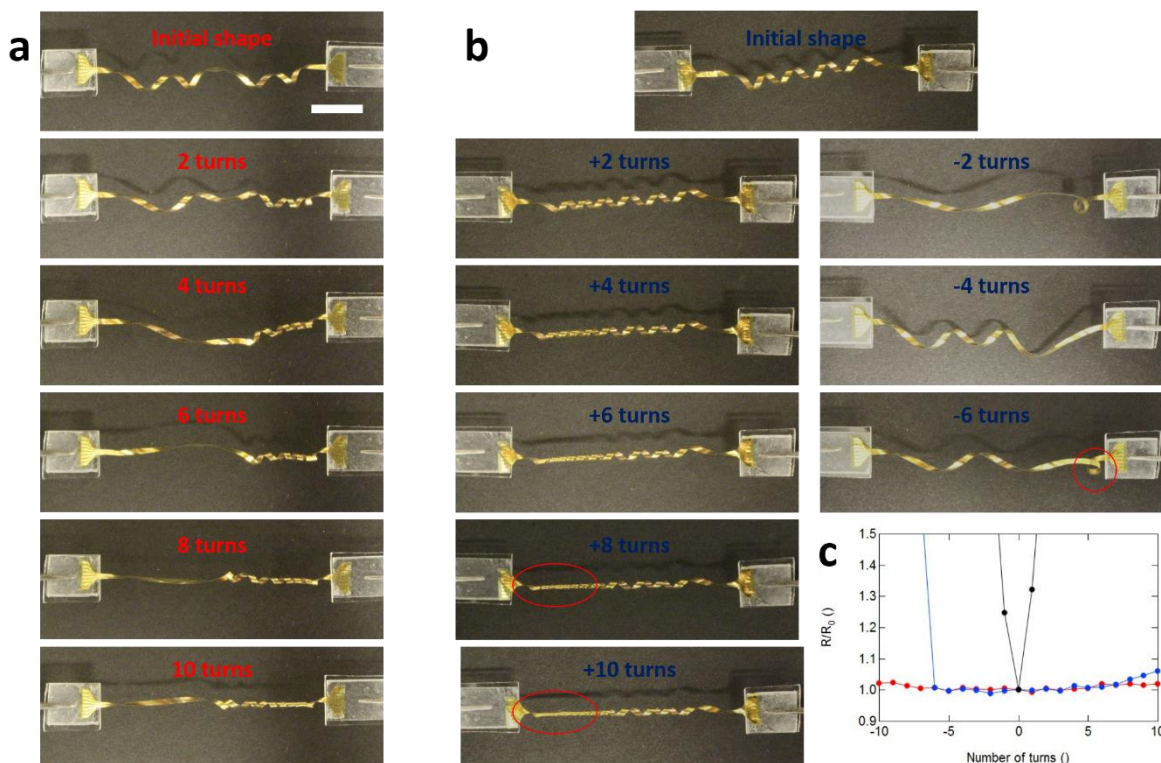


Figure S5. (a) Twisting deformation of helical inversion device. (b) Twisting deformation of helical device. + indicates direction of twisting to input more turns. - indicates twisting direction to release turns. (c) Resistance measurements by function of twisting deformation for helical inversion (red), helical (blue), and flat (black) device. (Scale bar = 1 cm)

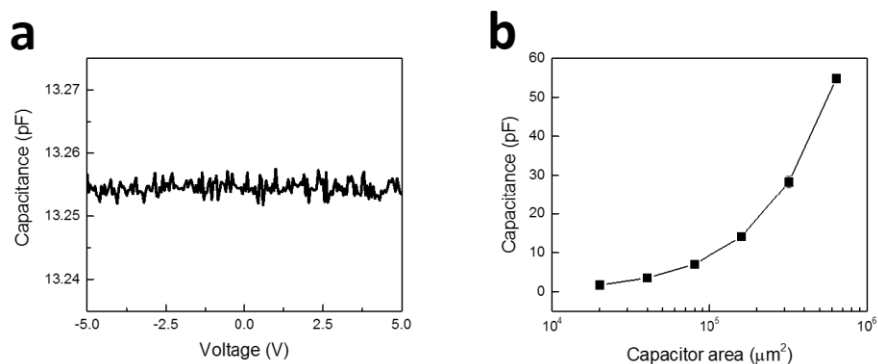


Figure S6. (a) Capacitance as function of voltage bias from -5 V to +5 V. Capacitance value of ~ 13.255 pF is maintained. (b) Scalable capacitances ranging from 1.7 to 55 pF have been achieved for various capacitor areas from 2×10^{-4} to $6.4 \times 10^{-3} \text{ cm}^2$.

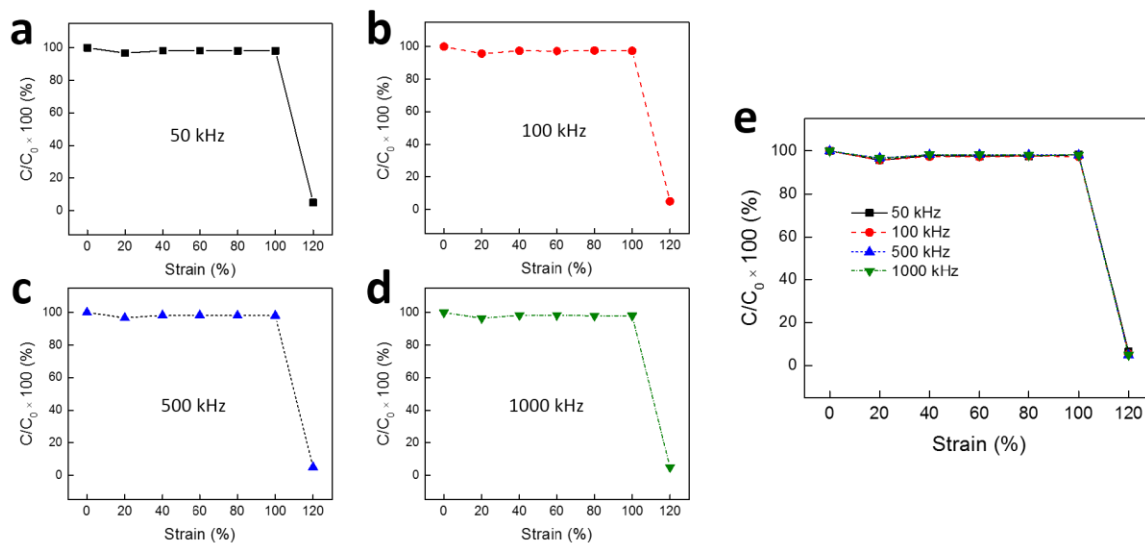


Figure S7. Capacitance as function of strain at (a) 50 kHz, (b) 100 kHz, (c) 500 kHz, (d) 1000 kHz, and (e) overlay.

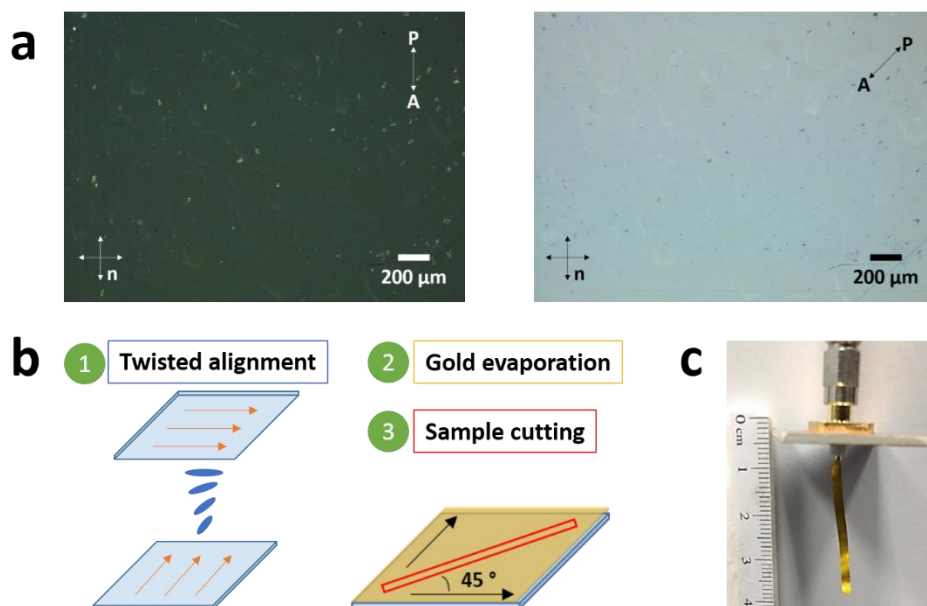


Figure S8. (a) Transmission polarized optical micrographs of twisted nematic LCE substrates used for antenna fabrication. (b) Schematic of LCE antenna fabrication procedure. (c) Prepared LCE antenna at room temperature.

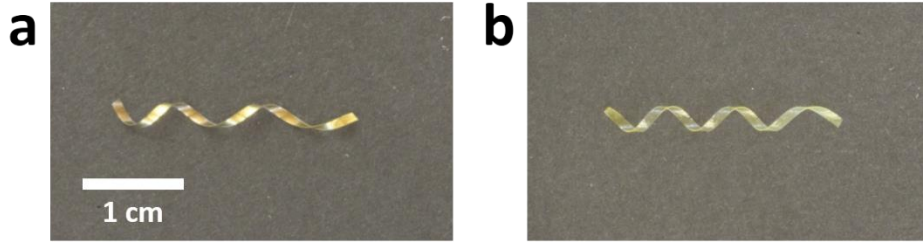


Figure S9. 3D helical shape of (a) conducting trace device (with metal) at room temperature. (b) LCE substrate (without metal) at room temperature.

Analysis of the skin depth and sheet resistance to determine gold thickness for antenna:

At high frequencies, the current density is concentrated into the region near the surface of a good conductor. This is commonly called the skin effect. Skin depth or penetration depth is defined as the depth below the surface of the conductor at which the amplitude of an incident electric field has decreased by factor $1/e$ (approximately 0.37). The skin depth, δ , can be calculated using

Equation S1.

$$\delta = \sqrt{\frac{\rho}{\pi f \mu_r \mu_0}} \quad (1)$$

Where ρ is the resistivity, f is the frequency, μ_r is the permeability of free space and μ_0 is the magnetic permeability of the conductor material. The metal thickness of our LCE antennas will not to exceed the skin-depth at the corresponding frequencies of operation since thick metallizations will not allow these antennas to change their shape. Therefore, thick metallizations will be avoided. In our case, the skin depth of the gold metallization is $0.940 \mu\text{m}$ at 7 GHz and it was calculated using the following parameters: $\rho = 2.44 \mu\Omega \text{ cm}$, $\mu_0 = 4\pi \times 10^{-7} \text{ H/m}$, and $\mu_r = 1$. The two operating frequencies of the LCE antenna at room temperature were 2.7 GHz and ~ 7 GHz. The thickness of the evaporated gold, t , is 200 nm, which is 13% and 21% of the skin depth, δ , at 2.7 GHz and ~ 7 GHz, respectively. The RF sheet resistance, R_s , of the 200 nm-thick

conductive gold layer is 0.13 Ω/sq and 0.135 Ω/sq , respectively at 2.7 GHz and 6.95 GHz according to the following **Equation S2**.

$$R_s = \frac{\rho}{\delta} \frac{1}{1 - e^{-t/\delta}} \quad (2)$$

Equation (2) shows that as the thickness of the gold layer increases the RF sheet resistance decreases thereby decreasing the RF losses of the antenna. In turn, increased RF losses in the antenna decrease its radiation efficiency; therefore, the metal layer should not be made too thin. However, the thicker the metallization becomes the more difficult the self-morphing of the metallized LCE becomes. The metallization should not be chosen too thick as this will restrict the ability of the LCE to change its shape. There is a performance trade-off in the design of the LCE antennas is controlled by the thickness of the metallization between RF losses and mechanical ability to self-morph. It was observed that LCEs with thinner metallization can change shape more easily, whereas LCEs with thicker metallization exhibit less RF resistive losses.

References

- (1) Rihani, R.; Kim, H.; Black, B.; Atmaramani, R.; Saed, M.; Pancrazio, J.; Ware, T. Liquid Crystal Elastomer-Based Microelectrode Array for In Vitro Neuronal Recordings. *Micromachines* **2018**, 9 (8), 416.
- (2) Yaroshchuk, O.; Reznikov, Y. Photoalignment of Liquid Crystals: Basics and Current Trends. *J. Mater. Chem.* **2012**, 22 (2), 286–300.