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METHOD ARTICLE

# REVISED Direct laser writing of liquid crystal elastomers oriented by a horizontal electric field

[version 2; peer review: 2 approved]

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## Abstract

**Background:** The ability to fabricate components capable of performing actuation in a reliable and controlled manner is one of the main research topics in the field of microelectromechanical systems (MEMS). However, the development of these technologies can be limited in many cases by 2D lithographic techniques employed in the fabrication process. Direct Laser Writing (DLW), a 3D microprinting technique based on two-photon polymerization, can offer novel solutions to prepare, both rapidly and reliably, 3D nano- and microstructures of arbitrary complexity. In addition, the use of functional materials in the printing process can result in the fabrication of smart and responsive devices.
**Methods:** In this study, we present a novel methodology for the printing of 3D actuating microelements comprising Liquid Crystal Elastomers (LCEs) obtained by DLW. The alignment of the mesogens was performed using a static electric field (1.7 V/μm) generated by indium-tin oxide (ITO) electrodes patterned directly on the printing substrates.
**Results:** When exposed to a temperature higher than 50°C, the printed microstructures actuated rapidly and reversibly of about 8% in the direction perpendicular to the director.
**Conclusions:** A novel methodology was developed that allows the printing of directional actuators comprising LCEs via DLW. To impart the necessary alignment of the mesogens, a static electric field was applied before the printing process by making use of flat ITO electrodes present on the printing substrates. The resulting microelements showed a reversible change in shape when heated higher than 50 °C.

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**Keywords**
Liquid Crystal Elastomers (LCEs), Microelectromechanical Systems (MEMS), Direct Laser Writing (DLW), Two-Photon Polymerization (2PP)

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**REVISED** **Amendments from Version 1**

This version include modification suggested by reviewers.

In particular, more details on experimental procedure have been added.

Moreover, the Introduction has been reviewed, improving the state of the art, and clarifying the scope of the work.

Finally, Figure 1, Figure 4, and Figure 5 have been improved.

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## Introduction

In recent decades, microelectromechanical systems (MEMS) have become a fundamental part of our technology and everyday life, playing a vital role in many diverse applications ranging from the automotive industry, to consumer electronics, the biomedical, and apparels sectors[1]. The downsizing of control and processing units to small components – usually ranging from few millimeters down to hundreds of nanometers – allows the fabrication of complex and effective systems of sensors and actuators which guarantee reliable performances and fast responses.

In most cases, MEMS devices are fabricated employing integrated circuits (IC) technologies which rely on 2D or 2.5D methodologies such as lithography, chemical and physical deposition, dry and wet etching, and thermal treatment just to mention the most common[2]. Whereas this has permitted this technology to achieve remarkable results, prototyping and optimization of IC technologies is expensive, both in terms of materials and equipment, and is generally slow.

Novel 3D microprinting techniques can help overcome these barriers, allowing fast prototyping and employing affordable materials[3–5]. In addition, they can enable the printing of fully 3D micro- and nanostructures of arbitrary complexity and shape[6], which is an interesting added value for MEMS fabrication. Among several approaches, Direct Laser Writing (DLW) based on two-photon polymerization technology, is a fully-3D microprinting technique which allows the fabrication of microstructures and architectures with resolutions down to 100 nm[7] and high speeds (in the order of tens of mm/s)[8,9].

This technique usually makes use of a fs-pulsed near infrared laser (NIR; more commonly, 780 nm) which is focused by means of optical elements inside a photoresist which is transparent to the laser wavelength and polymerize at shorter wavelengths. In the focus spot, the intensity of the radiation is sufficiently high to trigger two-photon absorption, a non-linear optical process in which a molecule can absorb two photons simultaneously to get in an excited state[10]. Such phenomenon can start the polymerization process which crosslink and solidify the material. By moving the laser focus in space, one can therefore obtain a 3D structure reliably and reproducibly. Nonetheless, despite these capabilities and the effort placed on research around DLW, to the best of our knowledge, only a few examples of actual MEMS fabricated (at least partly) using DLW can be found in the literature[11–13].

Next to the 3D geometrical freedom during the printing process, DLW also offers the possibility of employing a large plethora of functional materials which confer smart and active properties to the final structures[10]. For instance, responsive materials which can change their shape in response to a precise stimulus in a controlled and reproducible fashion, can act as actuators powered by light, heat, pH, solvent interaction, magnetic and electric fields[10]. The combination of DLW and complex functionalization is often referred to as 4D printing. Several recent reviews well-describe the state-of-the-art approaches to prepare and characterize actuating elements[14,15]. Of particular interest are materials that provide directional actuation, which can confer anisotropic motion to the different parts and components[16].

One strategy to achieve such control consists in the use of a bilayer of materials with different Young moduli (which in DLW can be simply achieve by varying the degree of cross-linking)[17], limiting the shape change and thereby induce bending[18]. The bilayer limits the geometrical freedom and for this reason materials that intrinsically provide directional actuation are of particular interest, as they can confer anisotropic motion to the different parts and components[19].

Liquid crystal elastomers (LCEs) are one of the most studied directional actuation materials because of their simple fabrication techniques, the possibility of using a vast array of molecules with different properties, and their power output[20–23]. LCEs are a class of polymeric materials obtained by the polymerization of rigid and rod-shaped liquid crystal (LC) molecules. If the monomer molecules are in a nematic (or smectic) phase while the polymerization takes place, the local order of the mesogens is partially retained in the final material. Then, upon heating, the loss of order creates a reversible shape change, shortening the elastomer along the director (and lengthening it along the other directions, as the shape change occurs at almost constant volume). The alignment of the LC moieties is crucial for the performances of the final device[24,25]. The former is usually achieved through surface rubbing[26,27], surface patterning and functionalization[28,29], mechanical stretching[30], polarized light[31], and electromagnetic fields[32,33].

Examples of LCE microstructures printed trough DLW have been reported, where DLW can trigger the polymerization of LC monomers functionalized with acrylate groups[25,27,34,35]. Most of them employed rubbing or surface modification to induce the alignment of the LC monomers[36–40]. In this way, however, the fabrication of the substrates is time consuming and needs to be tailored to the specific structure that one wants to print, limiting to a certain extent the rapid prototyping capability offered by DLW and preventing the use of mass-manufactured substrates. For example, Li *et al.* explored the tuning of

alignment by a weak magnetic field using LCE's cross-linked by diacrylates and applied them as light-intensity modulators, but did not combine the orientation method with 3D printing[19].

One may overcome these issues by making use of electric fields to generate differently aligned phases within the same substrate: by placing electrodes accordingly, one may fabricate, in a single step, a series of actuators characterized by different properties, direction of actuation, and working conditions (even along their z-axis). Tartan *et al*. investigated in several studies the behavior of DLW-printed LCE structures in presence of a vertical electric field[41,42]. Very recently, Münchinger *et al*. showed the possibilities offered by a multi vector quasi-static electric field[43]. Compared to the former – and also in combination with it –, the latter approach offers more practical possibilities for the fabrication of MEMS and functional structures, permitting the independent fabrication of actuators capable of produce motion in different directions within a single printing step. Notably, as we show in this study, horizontal alignment via an electric field, could also be achieved by employing flat electrodes. These latter can be printed or obtained through standard lithographic approaches directly on the substrate offering several advantages. For example, one can optimize the design of the substrate with minimum effort to match the requirement of the DLW printed devices by preparing a new design; at the same time, this approach offers a practical solution for scalability, since flat substrates with conductive paths on top can be easily mass produced. In addition, the possibility of preparing the electrodes directly on the printing substrate, makes this approach useful to be employed in most DLW machines, commercial or home built, as it does not require any extra modules. Moreover, as ultimate goal, this approach will make possible to reorient in real time the LCE during the DLW fabrication, allowing the creation of anisotropically aligned LCE domains in the same microstructures, thus allowing complex actuation patterns.

In this study, we report the use of DLW to fabricate several LCE microstructures to be used as actuators. We performed the alignment of the mesogens employing an electric field parallel to the substrate (1.7 V/μm) generated by applying bias to flat ITO electrodes prepared on the same glass substrate used for the printing process. The resulting structures were characterized by remarkable resolution and showed actuation when exposed to temperatures higher than 50 °C in analogy to macroscopic films prepared in the same manner.

## Methods

### Materials

The 2-methyl-1,4-phenylene bis(4-(3-(acryloyloxy)propoxy)benzoate) (RM257, LC-DA) and 4-((5-(acryloyloxy)pentyl)oxy)phenyl 4-methoxybenzoate (LC-MA) were obtained from SYNTHON Gmbh (Germany) and used as received. Photoinitiator Irgacure 369, chloroform, isopropanol, and hydrochloric acid 37% were obtained from SigmaAldrich (United Kingdom). Niric acid 75% was oobtained from CARLO ERBA Reagents (Italy, www.carloerbareagents.com). Indium-tin oxide (ITO)-coated glass slides (CEC020T, dimensions: 30±0.3, 0.175±0.015, resistance 10–20 Ω) were purchased from Tecnovetro (Italy). Photoresist AZ 10XT, developer and remover were acquired from Microchemicals Gmbh (Germany). Conductive silver paste (RS 186-3600) was obtained from RS Components (Italy). High voltage supply is obtained by using a P12P module by EMCO (France).

### Fabrication of indium-tin oxide interdigitated electrodes

ITO-coated glass slides were spuncoated with AZ 10XT (3400 rpm, 60 s, final thickness 10 μm) on a BLE Laboratory Equipment Delta 10 BM spincoater (Germany, b-l-e-laboratory-equipment.germanytrade.it) and soft baked at 120 °C for 100 s on a BLE Laboratory Equipment Delta 150 BM hotplate. A pattern of interdigitated electrodes was transferred onto the samples exposing them to UV radiation through a negative mask by means of a mask aligner (MA/BA6 SUSS MicroTec) employing the power dose suggested by the supplier (1500 mJ/cm$^2$). The exposed samples were developed for 20 minutes in AZ developer and rinsed thoroughly with water. Removal of the ITO was performed by immersion in freshly prepared aqua regia (1:3 $HNO_3$ 75%:HCl 37%) for 10 s. After rinsing with abundant water, the mask was removed by immersion in AZ Remover for five minutes and rinsing with isopropyl alcohol. Cu tape was added to facilitate the wiring and were contacted using silver paste. The ITO electrodes used in this study were 200 μm wide and comprised a gap of 150 μm.

### Direct laser writing of liquid crystal elastomer structures

The calculated amount of photoinitiator to achieve 7%mol. was dissolved in 0.5 mL of chloroform and added to a mixture of LC-DA and LC-MA in a vial to form a homogeneous solution. The formulations employed in this study comprised LC-MA:LC-DA mixtures in 8:2, 7:3, and 6:4 molar ratios. An example for the preparation an 8:2 resist mixture is the following: 2.2 mg of Irgacure 369 were dissolved in 1 mL of chloroform through stirring, after complete dissolution, 0.5 mL of the latter solution were employed to dissolve 14.6 mg of LC-MA and 5.4 mg of LC-DA. The solutions were kept in the dark.

For the preparation of the substrate, the mixture was then drop-casted on the ITO electrodes, covered to prevent light damage to the photoresist, and heated to 90 °C on a hotplate until melting was complete. A DC bias was applied (1.7 V/μm) and the hotplate cooled to 30°C at a rate of 5 °C/20 minutes. The samples were then rapidly transferred to a Photonic Professional system GT2 (Nanoscribe) which mounted a 780 nm laser to perform the printing process. For the latter, .stl files of the 3D models, consisting of pyramids, cubes cantilevers and square nails, were prepared using the free software Blender (v2.93) and processed for the 3D printing process by performing the slicing using the machine proprietary software (DeScribe). Hatching and slicing were set at 0.2 μm and 0.3 μm respectively. An oil immersion method as described in the manual of the supplier was used, mounting a 63x lens. A laser power of 20 mW (40% of nominal 50mW full power) and a laser speed of 10000 μm/s (equivalent to a "power dose" of 0.2 J/mm) were employed. After the printing, the structures were developed for 10 minutes in a 1:1 chloroform:isopropylalcohol solution and let dry in air.

### Evaluation of actuation properties

A substrate bearing the printed structure was placed over a Peltri element under an optical microscope (Hirox KH-8700 digital microscope) and repeatedly heated up to 70 °C and cooled down to room temperature (5 cycles). Measurements were taken using the image processing software of the instrument (KH-8700 v1.40a, HRMT v1.04).

### Simulations

All simulations were carried out in COMSOL Multiphysics 5.6. The purpose of the simulations was to illustrate that the electric field is sufficiently homogeneous under our conditions, and to show that the behavior observed in the material is consistent with what is expected from the theory and thus from simulation. The COMSOL simulations are therefore not critical for the reproducibility of the methodology presented above. A suitable open software alternative to reproduce the calculation could be OPENFoam, however, the authors did not test it.

Electric field simulation: we performed a 2D simulation using the AC/DC Module of COMSOL. We simulated a 400 µm wide section of the electrodes structure a 100 µm thick silica glass layer (relative permittivity of 2.09), on top of which is the 100 µm thick LC layer (relative permittivity of 3). On top and bottom are two layers of air (infinite domains). The electrodes are modelled as line boundaries, each 100 µm wide, at the glass-LC interface, placed at the two sides of the domain (leaving a 200 µm spacing between them. The condition of zero charge is applied to all external boundaries; to each electrode is applied an electric potential (+dV/2 to the left one and –dV/2 to the right one, where dV = 1250 V).

LCE structures simulations: we performed 3D simulations of the cube and nail structures using the Structural Mechanics Module of COMSOL. The geometries are imported from the corresponding .stl files. The LCE is modelled as a Linear Elastic Material with Young's Modulus E = 1 MPa, Poisson's ratio ν ~ 0.5 (nearly incompressible), and density ρ = 1.2 g/cm$^3$. As in Palagi *et al.*,[44] the thermal response of the LCE is simulated by defining the dependence of the order parameter q on temperature according to the function $q = Q_n\left(1+e^{\frac{T-T_{ni}}{\gamma}}\right)^{-1}$, where $Q_n$ is the order parameter of the nematic phase, which we set to 0.1, $T_{ni}$ is the nematic-to-isotropic transition temperature, which we set to 60°C, and γ is a parameters that defines the width in temperature of the transition (here we set γ = 3K)[45]. The active stretch of the LCE is then defined as $\lambda = \left(\frac{1+2q}{1-q}\right)^{\frac{1}{3}}\left(\frac{1+2Q_n}{1-Q_n}\right)^{-\frac{1}{3}}$. The strain along the director is then defined as $\varepsilon_Z = \frac{1}{2}(\lambda^2-1)$, whereas the strain along the two perpendicular directions is $\varepsilon_{XY} = \frac{1-\lambda}{2\lambda}$. These strains, which thus depend on temperature, are set as initial strain to the material. The structures have a fixed constraint on the bottom boundary. The LCE response is simulated by sweeping the temperature T between 40°C and 80°C with a step of 5°C.

The simulation results in .csv format are available in *Extended data*[46] for further independent analysis and post processing.

## Results and discussion

All optical microscopy and scanning electron microscope (SEM) images presented in this section are available in *Underlying data*[46].

The combination of the performances of LCE actuators with the unparalleled structural freedom offered by DLW at the micro/nano scale, can offer novel fascinating opportunities for the fabrication of functional MEMS.

In order to fully exploit the potential of DLW, however, one must be able to orient LCEs to fit their needs, and that includes the possibility of orienting the mesogens in different directions across the substrate. To achieve this goal, flat electrodes (which can be easily prepared by lithographic approaches or evaporation) can be designed to carefully pattern the substrate and control the orientation of polar mesogens by application of an appropriate bias as they will tend to align to the applied electric field[21]. While it is true that they cannot offer a homogeneous field perpendicular to the plane, its modulus only decreases of about 10% after 50 µm perpendicularly above the plane (Figure 1), thus still allowing the fabrication of reasonably tall structures.

We designed our interdigitated electrodes to be 200 µm wide and characterized by a pitch of 150 µm. Such distance is much larger than what employed by Tartan *et al.* in their work in ref. 41 (5 µm), it however enables us to envision more flexible fabrication procedures for functional MEMS of dimensions of several tens of microns in the future. These electrodes (which served as substrate for the printing process directly) were fabricated from ITO-coated glass slides by application of a photoresist mask, etching of the exposed ITO surface, and removal of the mask. Electric contact was realized through copper tape and conductive silver paste.

The LCs we employed (LC-DA and LC-MA) are shown in Figure 1a and were chosen for their relatively large dipole moment and because they are commonly used by several research groups for DLW[36,39,42]. When a melt comprising these compounds was cooled in the presence of an applied electric field of 1.7 V/µm, it tended to form large domains between the electrodes (Figure 1c–d and Supporting VideoZ1 in *Extended data*[46]). When we increased the bias beyond that threshold (e.g. 2.5 V/µm), we noticed the LC started to flow between the electrodes. Kuroboshi *et al.* recently described this phenomenon in a study about the behavior of electro-conjugate fluids between two electrodes at high bias[47]. Notably, the application of a bias high enough to trigger this effect, was enough to provoke the melting of the mesogens from the solid phase. Deposition of a 100 nm dielectric layer (Parylene C) prevented LCs motion at high biases. Unfortunately, it also hindered dramatically the alignment of the mesogens which responded only to alternate fields and did not form large uniform domains.

To align the mesogens and prepare the substrates for the micro-printing process, a mixture comprising the LCs and a photoinitiator was placed on the electrodes as prepared and melted at 90 °C on a hotplate. We applied 250 V (1.7 V/μm) and allowed the sample to cool down slowly to room temperature (-15 °C/h). We tried several different compositions and found that the formulation comprising a molar ratio of 7:3 LC-MA:LC-DA gave the best results for our scope. In particular, when compared to different mixtures, the printed structures showed an appreciable resolution (Figure 2) and resulted soft enough to observe the actuation (as discussed later and depicted in Figure 4). Increasing the amount of monoacrylate compound (8:2 LC-MA:LC-DA) resulted in structures that looked softer and less defined (see Figure 2), while increase of the quantity of difunctional LC (6:4 LC-MA:LC-DA) gave rise to more rigid structures that did not actuate appreciably.

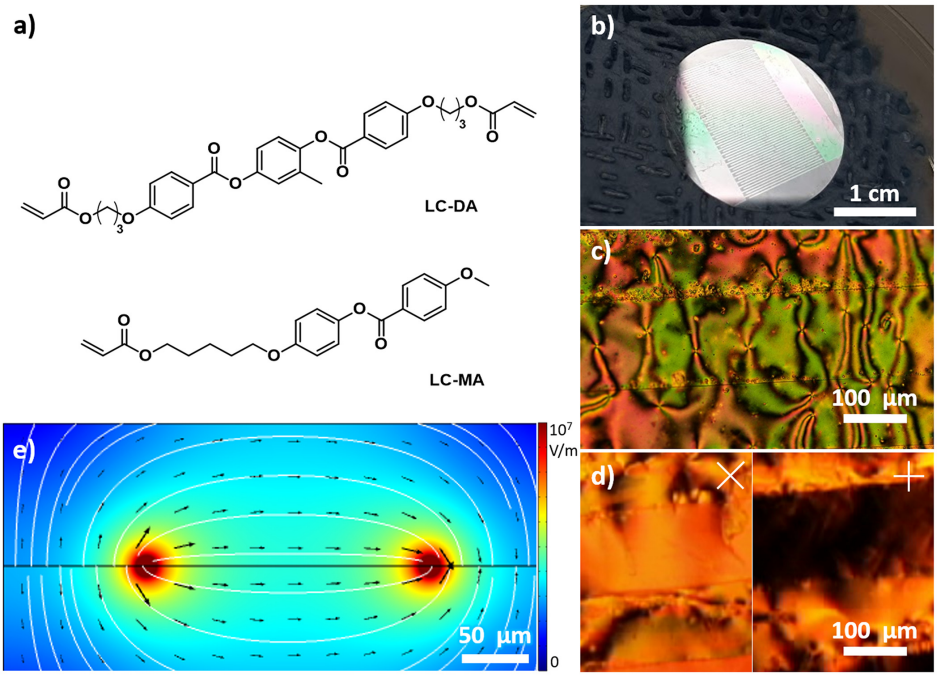



**Figure 1.** **a**) Molecular structures of the liquid crystal elastomers (LCE) monomers employed. **b**) Photograph of indium-tin oxide (ITO) interdigitated electrodes. **c**-**d**) Optical microscopy images of liquid crystals on substrate under cross polarizers no bias applied (**c**) and with bias applied (**d**; the white lines represent the orientation of the two polarizers). **e**) Simulation of the distribution of the electric field generated by flat electrode, view along the plane (cross section).

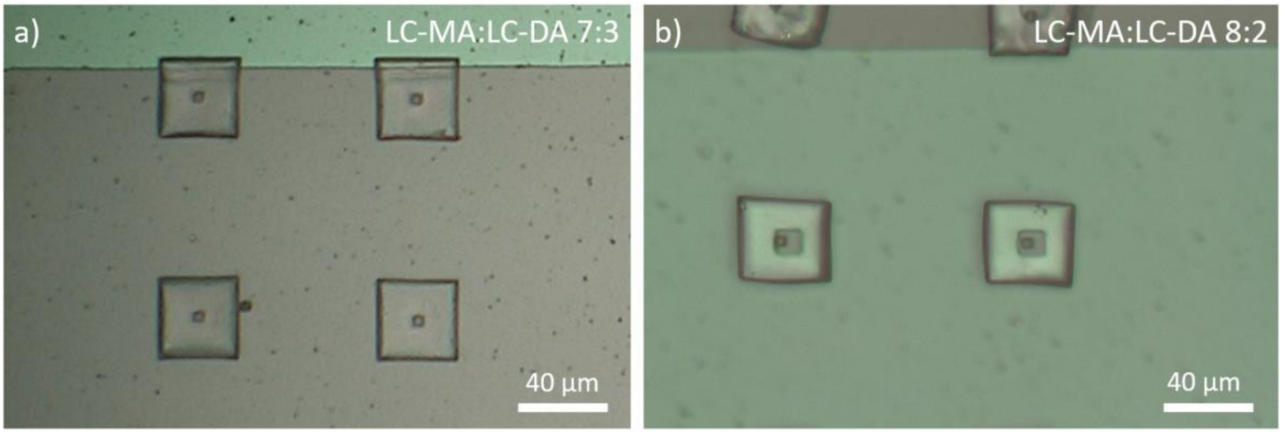



**Figure 2.** Optical microscopy images of micro nail structures realized using different formulations of 2-methyl-1,4-phenylene bis(4-(3-(acryloyloxy)propoxy)benzoate) (LC-DA) and 4-((5-(acryloyloxy)pentyl)oxy)phenyl 4-methoxybenzoate (LC-MA) : **a**) LC-MA:LC-DA molar ratio 7:3; **b**) LC-MA:LC-DA 8:2. An excess of monoacrylate component results in structures that look less defined and robust.

After several tests, the printing process was performed setting the laser power to 20 mW and the writing speed to $10^4$ µm/s (corresponding a power dose of 0.2 J/mm). Examples of microstructures (cubes, pyramids, and cantilevers) that it was possible to realize employing these conditions are shown in Figure 3. Remarkably, we observed minimal loss of focus and good resolution even for structures as tall as 50 µm despite the known birefringence of LC materials.

To evaluate the actuation performances, we printed cubes and 'square nails' microstructures (Figure 4 and Figure 5), which can deform in a predictable manner upon heating. Compared to the former, the nail is attached to the bottom of the substrate through a relatively small area, thus allowing a less constrained motion.

When perpendicular polarizers are used to observe these structures, they showed evidence of alignment along the direction of the electric field. Their arrangement was, however, not perfect, as one can see from the fact that the microstructures do not appear completely dark when one of the polarizers is parallel to the mesogens alignment direction. This observation could have been a consequence of the molecular structures and the composition of the formulation[48] (e.g. the presence of photoinitiator can affect the crystallinity) or a non-optimal alignment in the presence of the electric field generated by flat

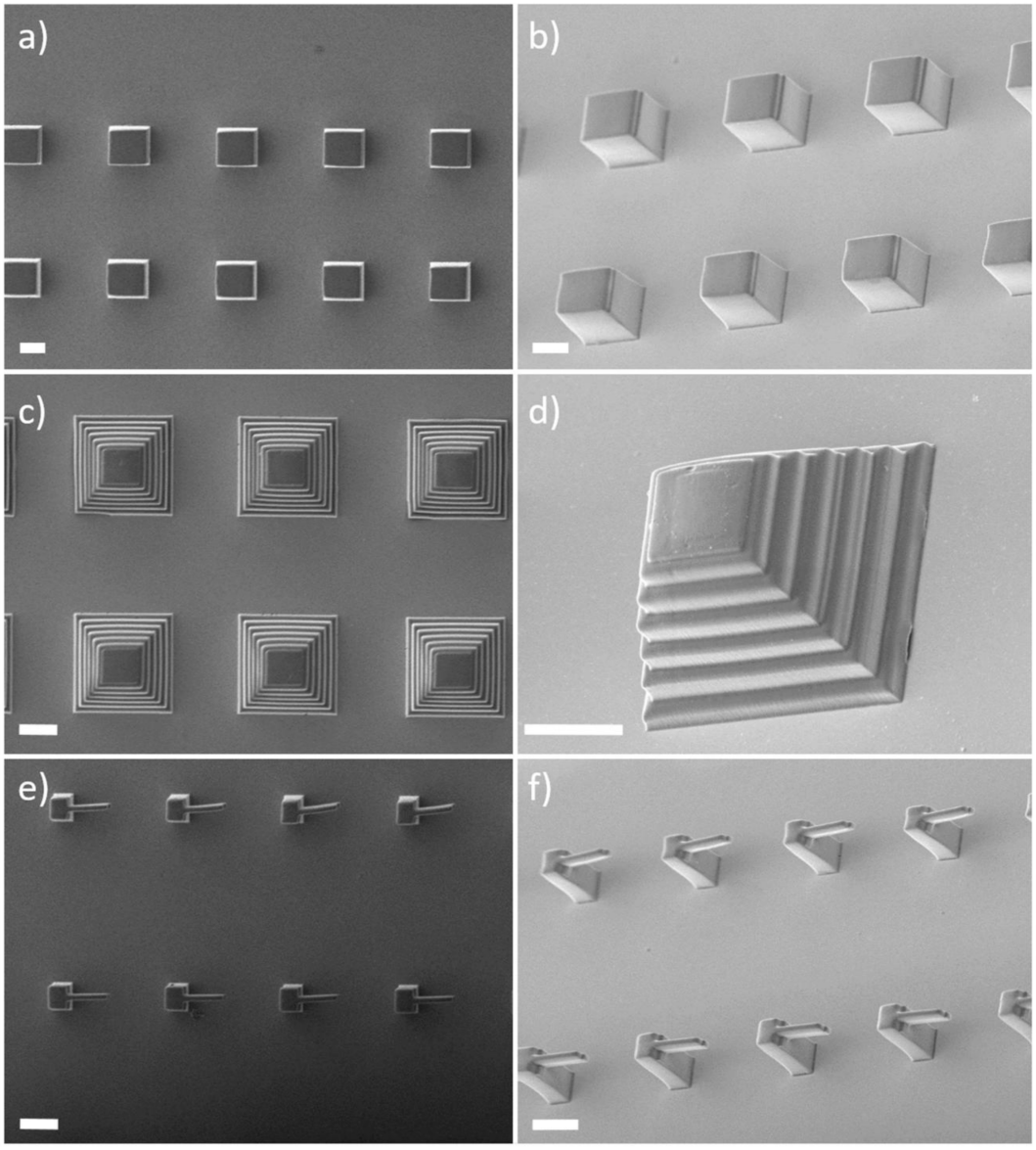



**Figure 3. a**, **b**) Scanning electron microscope (SEM) images (from above and sample tilted by 30°) of direct laser writing (DLW)-printed liquid crystal elastomers (LCE) microstructures comprising cubes, (**c**, **d**), 'Mayan' pyramids, (**e**, **f**), and cantilevers. Scale bars are 20 µm.

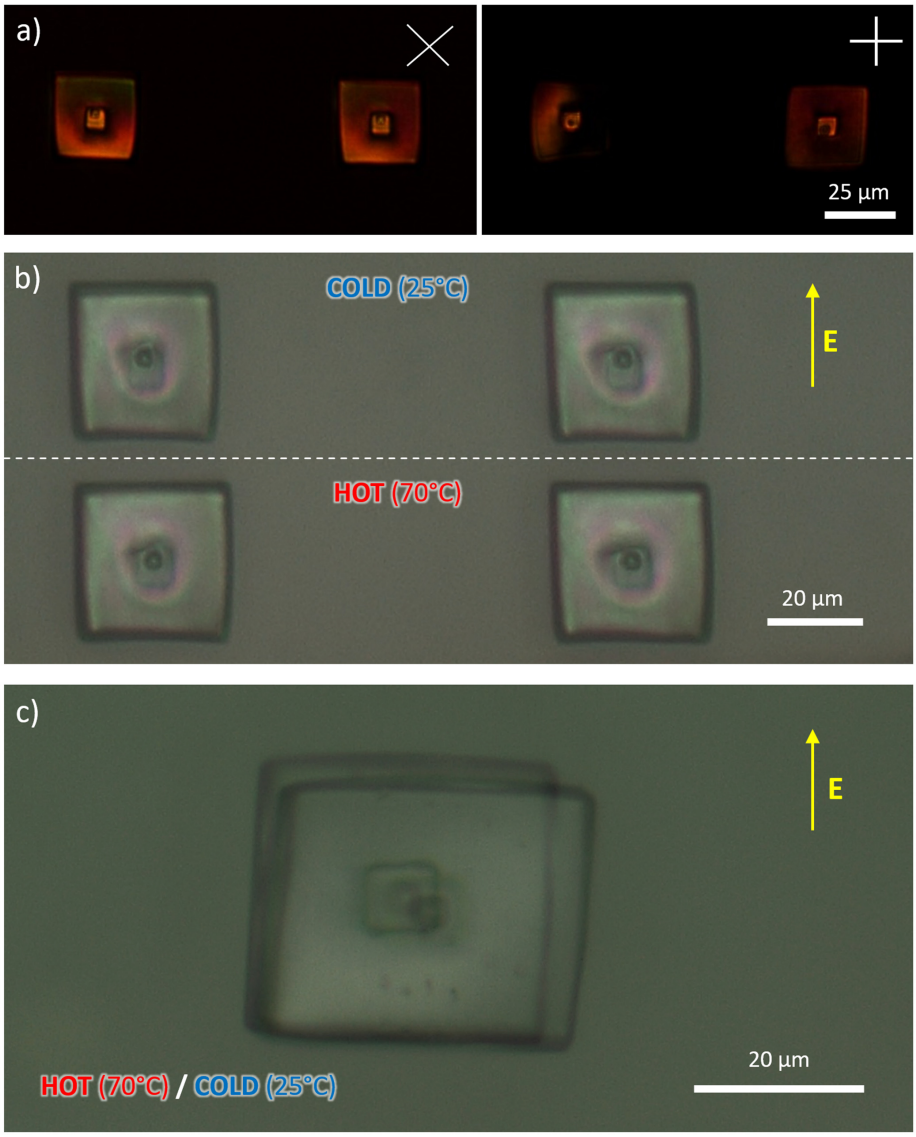



**Figure 4.** **a**) Optical microscopy images of micronails acquired through perpendicularly oriented polarizes placed at 45° and 0° with respect to the applied electric field **b**) Example of thermally responsive actuation of nail structures: comparison of images recorded at room temperature and at 70 °C; **c**) and superimposed images of a different nail at the aforementioned temperatures.

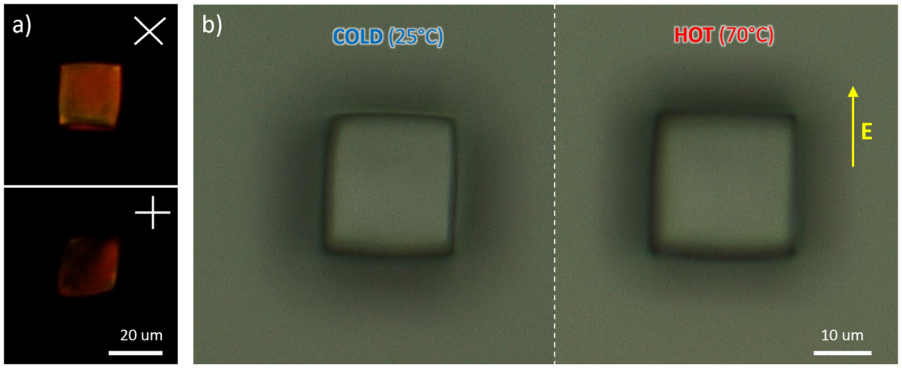



**Figure 5.** **a**) Optical microscopy images of microcubes acquired through perpendicularly oriented polarizes placed at 45° and 0° with respect to the applied electric field. **b**) Example of thermally responsive actuation via a comparison of images recorded at room temperature and at 70 °C.

electrodes. It could also be a result of the high energy printing conditions typical of 2PP (which may disrupt the molecular packing locally).

It is worth mentioning that the printing process in the presence of a bias, produced structures that do not replicate exactly the input design but appeared more compressed in the direction perpendicular to the director. While we do not know the origin of such discrepancy, a similar phenomenon was observed by Münchinger *et al.*,[43] and could be related to the DLW printing process.

Upon heating to a temperature above 50 °C, both DLW-printed nails and cubes changed their shape, shortening along the director of about 2.8±0.5% and 1.9±0.5% respectively, and lengthening in the perpendicular direction of about 8.3±0.5% and 7.3±0.5% respectively (Figure 4 and Figure 5, and Supporting VideoZ2; in *Extended data*[46] we also propose actuation of cantilevers, see Figure Z3). If we assume the lengthening along the z axis to be the same as the latter, we observe that the volume variation is not isovolumetric as it should be for LCEs[44]. Currently, we do not have any hypothesis on why this happens. Studies are currently ongoing to determine whether it is an effect arising from the printing parameters or intrinsic to the printed microstructures.

At about 70°C the actuation reached its maximum. Such deformations proceeded reliably and appeared to be fully reversible as it is common for LCE actuators. Indeed, as mentioned earlier, we found the degree of actuation to be larger for the nail structures compared to the solid cubes. The changes are, however, somewhat smaller than what can be expected from high-performance LCE systems[20]. This could be due to the limited alignment obtained in the case of this study, which, according to our simulations, resulted in an ordering parameter of about 0.1 (see Supporting Video Z3 and Z4 in *Extended data*[46]).

Unlike what reported by Münchinger *et al.*,[43] the actuation temperature was about 100 °C lower in our case (50 vs. 150 °C) despite the similar LC system employed. This difference could be related to higher amount of photoinitiator present in our formulation which can, in principle, affect the molecular characteristics of the crosslinked polymer by producing a larger number of shorter chains. This may affect several aspects of the final LCE, such as the overall crystallinity, the mechanical properties, and the transition temperature. Notably, the temperature of actuation was comparable to that of cm-long films prepared from an identical formulation and under the same electric field (see Figure Z2 in *Extended data*[46]). This suggests that the properties of the material dominate the behavior of the devices even in the case of DLW-printed components.

## Conclusions

In this study, we showed a methodology for the preparation of directional LCE micro-actuators of arbitrary shape that can be printed via DLW and employed as active component in MEMS. We made use of a flat electrode pattern to align a photoresist formulation (comprising polar liquid crystal mesogens and a photoinitiator) using a static electric field of 1.7 V/μm. The resist was prepared by mixing together photoinitiator (7% mol.) and two mesogens characterized by a single and a double acrylate groups. The alignment of the molecules was obtained by melting the resist mixture on the patterned substrate and allowing it to slowly cool down to room temperature under a DC bias before undergoing the DLW process.

Despite the use of a flat pattern, simulations showed that the field generated decreased of less than 10% even at 50 μm from the substrate plane, and thus it allows the DLW printing process of structures with a reasonable height with little restrictions. The printed actuators could reliably and reproducibly actuate when exposed to temperatures higher than 50°C (full actuation at 70°C), with a measured maximum displacement of about 8%. These limited performances of DLW-printed LCEs compared to those prepared by more common methodologies could be possibly related to the non-ideal alignment of the LC molecules in the elastomeric matrix (we estimated an ordering parameter of 0.1).

We are currently working to better the design of the electrodes and the fabrication process in order to improve the yield and performances of the printed actuators with the final goal of integrating this technology in the fabrication of functional MEMS and microdevices.

## Data availability

### Underlying data

Zenodo: Supporting information of paper "Direct Laser Writing of Liquid Crystal Elastomers Oriented by a Horizontal Electric Field". https://doi.org/10.5281/zenodo.5703137[46].

This project contains the following underlying data within in the file 'Underlying_data_Surce_Images.zip':

- Fig1c-20X.tif (source picture of Figure 1, panel c: optical microscopy image of liquid crystals on substrate under cross polarizers no bias applied. Magnification 20X).
- Fig1d-10X.tif (source picture of Figure 1, panel d: optical microscopy image of liquid crystals on substrate under cross polarizers with bias applied. Magnification 10X).
- Fig2a.tif (source picture of Figure 2, panel a: optical microscopy images of different microstructures realized using a LC-MA and LC-DA formulation with 7:3 ratio).
- Fig2b.tif (source picture of Figure 2, panel b: optical microscopy images of different microstructures realized using a LC-MA and LC-DA formulation with 8:2 ratio).
- Fig3a.tif (source picture of Figure 3, panel a: SEM images of DLW-printed LCE cube microstructures, top view).
- Fig3b.tif (source picture of Figure 3, panel b: SEM images of DLW-printed LCE cube microstructures, 30° sample tilted view).
- Fig3c.tif (source picture of Figure 3, panel c: SEM images of DLW-printed LCE 'Mayan' pyramid microstructures, top view).

- Fig3d.tif (source picture of Figure 3, panel d: SEM images of DLW-printed LCE 'Mayan' pyramid microstructures, 30° sample tilted view).

- Fig3e.tif (source picture of Figure 3, panel e: SEM images of DLW-printed LCE cantilevers microstructures, top view).

- Fig3f.tif (source picture of Figure 3, panel f: SEM images of DLW-printed LCE cantilevers microstructures, 30° sample tilted view).

- Fig4a-Left20X.tif (source picture of Figure 4, panel a, left position: optical microscopy images of LCE micronails acquired through perpendicularly oriented polarizes placed at 45° with respect to the applied electric field. Magnification 20X).

- Fig4a-Right20X.tif (source picture of Figure 4, panel a, right position: optical microscopy images of LCE micronails acquired through perpendicularly oriented polarizes placed at 0° with respect to the applied electric field. Magnification 20X).

- Fig4b-Bottom.tif (source picture of Figure 4, panel b, bottom position: optical microscopy images of LCE micronails, example of thermally responsive actuation of nail structures: image at 70 °C).

- Fig4b-Top.tif (source picture of Figure 4, panel b, top position: optical microscopy images of LCE micronails, example of thermally responsive actuation of nail structures: image at room temperature).

- Fig4c-Hot.tif (source picture of Figure 4, panel c, hot frame of superimposed image: optical microscopy images of LCE micronails, example of thermally responsive actuation of nail structures: image at 70 °C. High magnification).

- Fig4c-Cold.tif (source picture of Figure 4, panel c, cold frame of superimposed image: optical microscopy images of LCE micronails, example of thermally responsive actuation of nail structures: image at room temperature. High magnification).

- Fig5a-Top20X.tif (source picture of Figure 5, panel a, top position: optical microscopy images of LCE cube acquired through perpendicularly oriented polarizes placed at 45° with respect to the applied electric field. Magnification 20X).

- Fig5a-Bottom20X.tif (source picture of Figure 5, panel a, bottom position: optical microscopy images of LCE cube acquired through perpendicularly oriented polarizes placed at 0° with respect to the applied electric field. Magnification 20X).

- Fig5b-Right.tif (source picture of Figure 5, panel b, right position: optical microscopy images of LCE cube, example of thermally responsive actuation of nail structures: image at 70 °C).

- Fig5b-Left.tif (source picture of Figure 5, panel b, left position: optical microscopy images of LCE cube, example of thermally responsive actuation of nail structures: image at room temperature).

## Extended data

Zenodo: Supporting information of paper "Direct Laser Writing of Liquid Crystal Elastomers Oriented by a Horizontal Electric Field". https://doi.org/10.5281/zenodo.5703137[46].

This project contains the following extended data:

- Simulations.zip (Comsol Version 5.6 source simulation files for LCE microcube and LCE micronail upon heating, and for the electric field electric generated by flat electrode in experimental conditions. Complete Report file in PDF is also available, containing all the parameters and equations used for simulation. Finally, the simulation results are provided as text .csv files).

- SIVideo_LCAlignment.avi [Supporting VideoZ1] (video showing the response of the unpolymerized mesogens to an electric field of 1.7 V/μm).

- SIVideo_NailActuation.wmv [Supporting VideoZ2] (video showing the thermally activated actuation of a LCE nail microstructure upon several rt-75 °C cycles).

- SIVideo_SimluationCube.gif [Supporting VideoZ3] (video showing a simulation of the actuation of a LCE microcube upon heating).

- SIVideo_SimluationNail.gif [Supporting VideoZ4] (video showing a simulation of the actuation of a LCE micronail upon heating).

- ImageZ1.png [Supporting Figure Z1] (simulation of the distribution of the electric field generated by flat electrode, view along the plane, in cross section, with magnification of the central part of the working field).

- ImageZ2.png [Supporting Figure Z2] (photographs and thermal images of a LCE film obtained using a resin formulation identical to that employed in DLW on identical substrates that show the thermal response. Top: photograph of LCE films obtained by UV polymerization of a 7:3 LC-MA:LC-DA mixture over interdigitated flat ITO electrodes with an applied DC voltage. Upon heating with an infrared lamp (right column) the film bends and shortens. Middle: images acquired with a thermocamera highlighting the actuation temperature. Bottom: control LCE film polymerized as casted without electric field).

"ImageZ3.png" [Supporting Figure Z3]. a) Optical microscopy images of double-cantilever structure acquired through perpendicularly oriented polarizes placed at 45° with respect to the applied electric field. b) Example of thermally responsive actuation via a comparison of images recorded at room temperature (upper) and at 70 °C (bottom).

- Files_Blender_LCE.zip (Blender Version 2.93 source file (.blend) for microstructure fabrication and generated surface .stl files, including cube, nail, cantilever and pyramid geometries).

  "Cube Describe.zip". Example of DeScribe software output files containing all needed parameters used for printing cubes, generated starting from "cube.stl" file. Other geometries have been realised using the same writing parameters starting from appropriate ".stl" file.

Data are available under the terms of the Creative Commons Attribution 4.0 International license (CC-BY 4.0).

## References


1. Judy JW: **Microelectromechanical systems (MEMS): fabrication, design and applications.** *Smart Mater Struct.* 2001; **10**(6): 1115–1134.
Publisher Full Text
2. Lyshevski SE: **Mems and Nems**. CRC Press, 2018.
Publisher Full Text
3. Jones HB, Moore CP, Best AD, *et al.*: **Rapid prototyping MEMS using Laminated Resin Printing**. In *Emerging Digital Micromirror Device Based Systems and Applications XII.* (eds. Lee, B. L. & Ehmke, J.) SPIE, 2020; 6.
Publisher Full Text
4. Lifton VA, Lifton G, Simon S: **Options for additive rapid prototyping methods (3D printing) in MEMS technology.** *Rapid Prototyp J.* 2014; **20**(5): 403–412.
Publisher Full Text
5. Farahani RD, Dubé M: **Printing Polymer Nanocomposites and Composites in Three Dimensions.** *Adv Eng Mater.* 2018; **20**(2): 1700539.
Publisher Full Text
6. Bernardeschi I, Ilyas M, Beccai L: **A Review on Active 3D Microstructures via Direct Laser Lithography.** *Adv Intell Syst.* 2021; **3**(9): 2100051.
Publisher Full Text
7. Seniutinas G, Weber A, Padeste C, *et al.*: **Beyond 100 nm resolution in 3D laser lithography — Post processing solutions.** *Microelectron Eng.* 2018; **191**: 25–31.
Publisher Full Text
8. Spiegel CA, Hippler M, Münchinger A, *et al.*: **4D Printing at the Microscale.** *Adv Funct Mater.* 2019; **30**(26): 1907615.
Publisher Full Text
9. Lin Y, Xu J: **Microstructures Fabricated by Two-Photon Polymerization and Their Remote Manipulation Techniques: Toward 3D Printing of Micromachines.** *Adv Opt Mater.* 2018; **6**(8): 1701359.
Publisher Full Text
10. Carlotti M, Mattoli V: **Functional Materials for Two-Photon Polymerization in Microfabrication.** *Small.* 2019; **15**(40): e1902687.
PubMed Abstract | Publisher Full Text
11. Jayne RK, Stark TJ, Reeves JB, *et al.*: **Dynamic Actuation of Soft 3D Micromechanical Structures Using Micro-Electromechanical Systems (MEMS).** *Adv Mater Technol.* 2018; **3**(3): 1700293.
Publisher Full Text
12. Tricinci O, Carlotti M, Desii A, *et al.*: **Two-step MEMS microfabrication via 3D direct laser lithography**. In *Advanced Fabrication Technologies for Micro/Nano Optics and Photonics XIV.* (eds. von Freymann, G., Blasco, E. & Chanda, D.) SPIE, 2021; **11696**: 17.
Publisher Full Text
13. Kim S, Velez C, Pierre RS, *et al.*: **A Two-Step Fabrication Method for 3D Printed Microactuators: Characterization and Actuated Mechanisms.** *J Microelectromechanical Syst.* 2020; **29**(4): 544–552.
Publisher Full Text
14. Bunea AI, Martella D, Nocentini S, *et al.*: **Light-Powered Microrobots: Challenges and Opportunities for Hard and Soft Responsive Microswimmers.** *Adv Intell Syst.* 2021; **3**(4): 2000256.
Publisher Full Text
15. Nocentini S, Martella D, Parmeggiani C, *et al.*: **3D Printed Photoresponsive Materials for Photonics.** *Adv Opt Mater.* 2019; **7**(16): 1900156.
Publisher Full Text
16. Hippler M, Blasco E, Qu J, *et al.*: **Controlling the shape of 3D microstructures by temperature and light.** *Nat Commun.* 2019; **10**(1): 232.
PubMed Abstract | Publisher Full Text | Free Full Text
17. Ji Q, Moughames J, Chen X, *et al.*: **4D Thermomechanical metamaterials for soft microrobotics.** *Commun Mater.* 2021; **2**: 93.
Publisher Full Text
18. Nishiguchi A, Zhang H, Schweizerhof S, *et al.*: **4D Printing of a Light-Driven Soft Actuator with Programmed Printing Density.** *ACS Appl Mater Interfaces.* 2020; **12**(10): 12176–12185.
PubMed Abstract | Publisher Full Text | Free Full Text
19. Li S, Librandi G, Yao Y, *et al.*: **Controlling Liquid Crystal Orientations for Programmable Anisotropic Transformations in Cellular Microstructures.** *Adv Mater.* 2021; **33**(42): 2105024.
PubMed Abstract | Publisher Full Text
20. Kularatne RS, Kim H, Boothby JM, *et al.*: **Liquid crystal elastomer actuators: Synthesis, alignment, and applications.** *J Polym Sci Part B Polym Phys.* 2017; **55**(5): 395–411.
Publisher Full Text
21. Dierking I: **Nanoscience with liquid crystals.** *Liquid Crystals Today.* 2017; **26**(3): 63–65.
Publisher Full Text
22. de Jeu WH: **Liquid Crystal Elastomers: Materials and Applications**. Springer Berlin Heidelberg, 2012; **250**.
Publisher Full Text
23. Ambulo CP, Tasmim S, Wang S, *et al.*: **Processing advances in liquid crystal elastomers provide a path to biomedical applications.** *J Appl Phys.* 2020; **128**(14): 140901.
PubMed Abstract | Publisher Full Text | Free Full Text
24. Kowalski BA, Guin TC, Auguste AD, *et al.*: **Pixelated Polymers: Directed Self Assembly of Liquid Crystalline Polymer Networks.** *ACS Macro Lett.* 2017; **6**(4): 436–441.
Publisher Full Text
25. Nocentini S, Riboli F, Burresi M, *et al.*: **Three-Dimensional Photonic Circuits in Rigid and Soft Polymers Tunable by Light.** *ACS Photonics.* 2018; **5**: 3222–3230.
Reference Source
26. Zhang M, Shahsavan H, Guo Y, *et al.*: **Liquid-Crystal-Elastomer-Actuated Reconfigurable Microscale Kirigami Metastructures.** *Adv Mater.* 2021; **33**(25): e2008605.
PubMed Abstract | Publisher Full Text
27. Nocentini S, Martella D, Parmeggiani C, *et al.*: **Structured Optical Materials Controlled by Light.** *Adv Opt Mater.* 2018; **6**(15): 1800167.
Publisher Full Text
28. Guo Y, Shahsavan H, Sitti M: **3D Microstructures of Liquid Crystal Networks with Programmed Voxelated Director Fields.** *Adv Mater.* 2020; **32**(38): e2002753.
PubMed Abstract | Publisher Full Text | Free Full Text
29. McCracken JM, Tondiglia VP, Auguste AD, *et al.*: **Microstructured Photopolymerization of Liquid Crystalline Elastomers in Oxygen-Rich Environments.** *Adv Funct Mater.* 2019; **29**(40): 1903761.
Publisher Full Text
30. Zhang C, Lu X, Fei G, *et al.*: **4D Printing of a Liquid Crystal Elastomer with a Controllable Orientation Gradient.** *ACS Appl Mater Interfaces.* 2019; **11**(47): 44774–44782.
PubMed Abstract | Publisher Full Text
31. Ware TH, McConney ME, Wie JJ, *et al.*: **Actuating materials. Voxelated liquid crystal elastomers.** *Science.* 2015; **347**(6225): 982–984.
PubMed Abstract | Publisher Full Text
32. Tabrizi M, Ware TH, Shankar MR: **Voxelated Molecular Patterning in Three-Dimensional Freeforms.** *ACS Appl Mater Interfaces.* 2019; **11**(31): 28236–28245.
PubMed Abstract | Publisher Full Text
33. Yao Y, Waters JT, Shneidman AV, *et al.*: **Multiresponsive polymeric microstructures with encoded predetermined and self-regulated deformability.** *Proc Natl Acad Sci U S A.* 2018; **115**(51): 12950–12955.
PubMed Abstract | Publisher Full Text | Free Full Text
34. del Pozo M, Sol JAHP, Schenning APHJ, *et al.*: **4D Printing of Liquid Crystals: What's Right for Me?** *Adv Mater.* 2021; e2104390.
PubMed Abstract | Publisher Full Text
35. De Bellis I, Ni B, Martella D, *et al.*: **Color Modulation in *Morpho* Butterfly Wings Using Liquid Crystalline Elastomers.** *Adv Intell Syst.* 2020; **2**(9): 2000035.
Publisher Full Text
36. del Pozo M, Delaney C, Bastiaansen CWM, *et al.*: **Direct Laser Writing of Four-Dimensional Structural Color Microactuators Using a Photonic Photoresist.**

*ACS Nano.* 2020; **14**(8): 9832–9839.
**PubMed Abstract** | **Publisher Full Text** | **Free Full Text**

37. Woska S, Münchinger A, Beutel D, *et al.*: **Tunable photonic devices by 3D laser printing of liquid crystal elastomers**. 2020; **10**(11): 2928–2943.
**Publisher Full Text**

38. Zeng H, Martella D, Wasylczyk P, *et al.*: **High-Resolution 3D Direct Laser Writing for Liquid-Crystalline Elastomer Microstructures.** *Adv Mater.* 2014; **26**(15): 2319–2322.
**PubMed Abstract** | **Publisher Full Text**

39. Zeng H, Wasylczyk P, Parmeggiani C, *et al.*: **Light-Fueled Microscopic Walkers.** *Adv Mater.* 2015; **27**(26): 3883–3887.
**PubMed Abstract** | **Publisher Full Text** | **Free Full Text**

40. De Bellis I, Nocentini S, Santi MGD, *et al.*: **Two-Photon Laser Writing of Soft Responsive Polymers via Temperature-Controlled Polymerization.** *Laser Photon Rev.* 2021; **15**(8): 2100090.
**Publisher Full Text**

41. Tartan CC, Salter PS, Wilkinson TD, *et al.*: **Generation of 3-dimensional polymer structures in liquid crystalline devices using direct laser writing.** *RSC Adv.* 2017; **7**(1): 507–511.
**Publisher Full Text**

42. Tartan CC, Sandford O'Neill JJ, Salter PS, *et al.*: **Read on Demand Images in Laser-Written Polymerizable Liquid Crystal Devices.** *Adv Opt Mater.* 2018; **6**(20): 1800515.
**Publisher Full Text**

43. Münchinger A, Hahn V, Beutel D, *et al.*: **Multi-Photon 4D Printing of Complex Liquid Crystalline Microstructures by In Situ Alignment Using Electric Fields.** *Adv Mater Technol.* 2021; 2100944.
**Publisher Full Text**

44. Palagi S, Singh DP, Fischer P: **Light-Controlled Micromotors and Soft Microrobots.** *Adv Opt Mater.* 2019; **7**(16): 1900370.
**Publisher Full Text**

45. Palagi S, Mark AG, Reigh SY, *et al.*: **Structured light enables biomimetic swimming and versatile locomotion of photoresponsive soft microrobots.** *Nat Mater.* 2016; **15**(6): 647–653.
**PubMed Abstract** | **Publisher Full Text**

46. Carlotti M, Tricinci O, Den Hoed F, *et al.*: **Supporting information of paper "Direct Laser Writing of Liquid Crystal Elastomers Oriented by a Horizontal Electric Field"**. [Data set]. *Zenodo.* 2021.
**http://www.doi.org/10.5281/zenodo.5703137**

47. Kuroboshi Y, Takemura K, Edamura K: **Understanding of electro-conjugate fluid flow with dibutyl decanedioate using numerical simulation—Calculating ion mobility using molecular dynamics simulation.** *Sens Actuators B Chem.* 2018; **255**(1): 448–453.
**Publisher Full Text**

48. Yasuoka H, Takahashi KZ, Fukuda J, *et al.*: **Molecular architecture dependence of mesogen rotation during uniaxial elongation of liquid crystal elastomers.** *Polymer (Guildf).* 2021; **229**: 123970.
**Publisher Full Text**

# Open Peer Review

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**Version 2**

Reviewer Report 23 November 2021

https://doi.org/10.21956/openreseurope.15449.r28065

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✔ **Daniele Martella**
Istituto Nazionale di Ricerca Metrologica INRiM, Turin, Italy

In the revised version, the authors improve both state-of-the-art, scope and discussion of the experimental results. I believe the article is now more clear and complete. Also non specialized readers can understand the findings of this research.

***Competing Interests:*** No competing interests were disclosed.

***Reviewer Expertise:*** liquid crystal elastomer, direct laser writing, polymer chemistry, photoswitches

**I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard.**

Reviewer Report 22 November 2021

https://doi.org/10.21956/openreseurope.15449.r28064

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✔ **Ada-Ioana Ada-Ioana**
National Centre for Nano Fabrication and Characterization (DTU Nanolab), Technical University of Denmark, Lyngby, Denmark

The authors addressed the comments from myself and the other reviewer in a suitable manner. There are a few typos in the text that should be corrected, if possible.

***Competing Interests:*** No competing interests were disclosed.

***Reviewer Expertise:*** Two-photon polymerization direct laser writing.

**I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard.**

**Version 1**

Reviewer Report 03 November 2021

https://doi.org/10.21956/openreseurope.15240.r27908

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**Daniele Martella**
[1] Istituto Nazionale di Ricerca Metrologica INRiM, Turin, Italy
[2] Istituto Nazionale di Ricerca Metrologica INRiM, Turin, Italy

The authors describe the fabrication of DLW microstructures made by Liquid Crystalline Elastomers (LCEs). Thanks to the monomer alignment by electric field, the microstructures are able to deform under heating.

The article is easy to understand and clear but before it passes peer review, I recommend a more detailed analysis of the state-of-the-art. Many applications have been already demonstrated for light driven or humidity responsive actuators (e.g. by Wiersma, Sitti and Schenning group, some relevant papers are already present in the article) and photonic devices (e.g. the following papers on which I am a co-author *ACS Photonics*, 2018, *5*(8), 3222-3230; *Advanced Optical Materials*, 2018, *6* (15), 1800167).

Also the scope of the article has to be clarified. Since homogeneous planar alignment can be achieved with other simple techniques on large area (several cm), what are the advantages of the presented approach? What are the main differences with other setup that uses electric field for LC alignment?

Other technical comment to improve the manuscript are listed below:

1. Introduction: “If the monomer molecules are in a smectic of nematic phase” has to be corrected in “If the monomer molecules are in nematic phase”. Both monomers form only nematic phase.

2. Figure 1: I suggest to explain better the POM figures in panel b and c since the alignment is a key point of this article. In particular, the author can show the homogeneous planar alignment by rotating the sample under the cross polarizer.

3. In the phrase: “We tried several different compositions and found that the formulation comprising a 7:3 LC-MA:LC-DA” what is the ratio 7:3? A mol/mol percentage? The author should cite the paper “*Materials* **2016**, *9*(7), 525” talking about resolution with different crosslinker ratio.

4. Figure 3: the author should add the POM images of some 3D structures. Since they show poor alignment in the case of a cube, what is the resulting alignment in more complex structure (as the cantilever)?

5. Figure 4: even if the contraction is limited, the temperature decrease in the actuation with respect to previous articles is very interesting. By the way, the monomer composition is very similar to the ones previously reported and the alignment affects more the type and extent of deformation rather than the actuation temperature. The authors should clarify this point that, in my opinion, is related to the chemical structure of the polymer. The main difference with the literature is the very high amount of photoinitiator (7% mol/mol). I suggest the author to investigate how this parameter affect the deformation temperature (also in future studies).

**References**

1. Nocentini S, Riboli F, Burresi M, Martella D, et al.: Three-Dimensional Photonic Circuits in Rigid and Soft Polymers Tunable by Light. *ACS Photonics*. 2018; **5** (8): 3222-3230 Publisher Full Text
2. Nocentini S, Martella D, Parmeggiani C, Zanotto S, et al.: Structured Optical Materials Controlled by Light. *Advanced Optical Materials*. 2018; **6** (15). Publisher Full Text
3. Nocentini S, Martella D, Parmeggiani C, Wiersma DS: Photoresist Design for Elastomeric Light Tunable Photonic Devices.*Materials (Basel)*. 2016; **9** (7). PubMed Abstract | Publisher Full Text

**Is the rationale for developing the new method (or application) clearly explained?**

Yes

**Is the description of the method technically sound?**

Yes

**Are sufficient details provided to allow replication of the method development and its use by others?**

Yes

**If any results are presented, are all the source data underlying the results available to ensure full reproducibility?**

Yes

**Are the conclusions about the method and its performance adequately supported by the findings presented in the article?**

Yes

***Competing Interests:*** No competing interests were disclosed.

***Reviewer Expertise:*** liquid crystal elastomer, direct laser writing, polymer chemistry, photoswitches

**I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.**

Author Response 16 Nov 2021

**Virgilio Mattoli**

**REPLY TO REVIEWER 2 COMMENTS** – (Reviewer's comments in italics)
*The authors describe the fabrication of DLW microstructures made by Liquid Crystalline Elastomers (LCEs). Thanks to the monomer alignment by electric field, the microstructures are able to deform under heating.*
*The article is easy to understand and clear but before it passes peer review, I recommend a more detailed analysis of the state-of-the-art. Many applications have been already demonstrated for light driven or humidity responsive actuators (e.g. by Wiersma, Sitti and Schenning group, some relevant papers are already present in the article) and photonic devices (e.g. the following papers on which I am a co-author ACS Photonics, 2018, 5(8), 3222-3230; Advanced Optical Materials, 2018, 6(15), 1800167).*
**Author Reply:** As already mentioned concerning the previous reviewer, we expanded the introduction adding the suggested papers and other DLW studies on LCEs and actuators.

*Also the scope of the article has to be clarified. Since homogeneous planar alignment can be achieved with other simple techniques on large area (several cm), what are the advantages of the presented approach? What are the main differences with other setup that uses electric field for LC alignment?*
**Author Reply:** The advantage concerning the use of flat electrodes over other – even simpler – methods consists in the possibility to provide selective (and not necessarily parallel) alignment in different region of the sample. By devising an appropriate electrode pattern, it is possible to print in a single printing step LCEs structures with different orientations. We are planning to use this approach in a follow up study about the fabrication of MEMS comprising LCEs actuators. Compared to other ways to apply electric fields, flat electrodes and lateral fields, can be prepared easily and with high throughput using standard lithographic techniques, they are easy to implement in the DLW machines, and do not pose any strong limit to height of the structures that can be build. Moreover, as ultimate goal, this approach will make possible to reorient in real time the LCE during the DLW fabrication, allowing the creation of anisotropically aligned LCE domains in the same microstructures, thus allowing complex actuation patterns. We made these points clearer in the introduction and in the text.

*Other technical comment to improve the manuscript are listed below: Introduction: "If the monomer molecules are in a smectic of nematic phase" has to be corrected in "If the monomer molecules are in nematic phase". Both monomers form only nematic phase.*
**Author Reply:** The sentence was intended to refer to LC compounds in general, not limited to those used. 'Smectic' was therefore placed between brackets.

*Figure 1: I suggest to explain better the POM figures in panel b and c since the alignment is a key point of this article. In particular, the author can show the homogeneous planar alignment by rotating the sample under the cross polarizer.*
**Author Reply:** As the reviewer suggested, we added a picture of the same sample recorded with one polarizer aligned with the electric field.

*In the phrase: "We tried several different compositions and found that the formulation comprising a 7:3 LC-MA:LC-DA" what is the ratio 7:3? A mol/mol percentage? The author should cite the paper "Materials 2016, 9(7), 525" talking about resolution with different crosslinker ratio.*
**Author Reply:** The reviewer is indeed correct in pointing out that there was a missing detail. As they assumed, the ratio was indeed in moles. We added that information throughout the text.

*Figure 3: the author should add the POM images of some 3D structures. Since they show poor alignment in the case of a cube, what is the resulting alignment in more complex structure (as the cantilever)?*
**Author Reply:** Thin cantilever structures actuate less reliably, probably also because of the low young modulus, and were not included in the manuscript. We decided, however, to include an example in the Extended data as Figure Z3 (with reference in the main text). Unfortunately, the image we provided was recorded using only one configuration of the polarizers (45 deg) and we won't be able to repeat the experiments anytime soon.

*Figure 4: even if the contraction is limited, the temperature decrease in the actuation with respect to previous articles is very interesting. By the way, the monomer composition is very similar to the ones previously reported and the alignment affects more the type and extent of deformation rather than the actuation temperature. The authors should clarify this point that, in my opinion, is related to the chemical structure of the polymer. The main difference with the literature is the very high amount of photoinitiator (7% mol/mol). I suggest the author to investigate how this parameter affect the deformation temperature (also in future studies).*
**Author Reply:** The reviewer suggested an interesting take that we did not consider while writing the manuscript. Indeed, the amount of photoinitiator present in the polymerized structures can affect several characteristics of the LCE such as the overall crystallinity, the mechanical properties, and the transition temperature. We included this thought in the main text, despite the fact that we currently cannot either prove or disprove the role of the photoinitiator in the lower actuation temperature compared to other studies. It still remains an interesting study for the future.

***Competing Interests:*** No competing interests were disclosed.

Reviewer Report 29 October 2021

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**Ada-Ioana Ada-Ioana**
[1] National Centre for Nano Fabrication and Characterization (DTU Nanolab), Technical University of Denmark, Lyngby, Denmark
[2] National Centre for Nano Fabrication and Characterization (DTU Nanolab), Technical University of Denmark, Lyngby, Denmark

The article from Carlotti *et al.* describes the direct laser writing (DLW) of liquid crystal elastomer (LCE) microactuators which exhibit a reversible shape change of <10 % when actuated using heating (70C) / cooling (25C) cycles. The authors employed static electric fields to align the LCE mesogens before the DLW process and performed simulations to understand and verify their experimental results.

DLW of LCE has been explored by various groups, so the novelty of the work is not very high, but it is reasonable for a Methods article. However, the experimental procedures are not described in sufficient details, especially for a Methods paper, and some of the data necessary to reproduce this work is missing. Furthermore, the introduction of the work is rather short, slightly misleading at times, and is missing some important articles from literature.

I believe the article by Carlotti *et al.* is overall reasonably interesting and could be useful to the LCE DLW community. My detailed suggestions for improvement are listed below.

**Introduction**

I believe that the introduction talks too much about MEMS and not enough about other relevant aspects, especially given the fact that the fabricated microactuators have potential for MEMS, but are not exactly MEMS by themselves. This is somewhat addressed in the Conclusions section. I suggest expanding the introduction to cover relevant aspect of DLW and reported applications of LCE patterned by DLW. Furthermore, I suggest mentioning that this paper is actually about 4D printing, since the fabricated structures are responsive to external stimuli.

I suggest taking inspiration (and referencing) the following papers:

- https://doi.org/10.1002/aisy.202000256 and https://doi.org/10.1002/adom.201900156 - review papers covering microactuators prepared by LCE DLW.
- https://doi.org/10.1021/acsami.0c02781 , https://doi.org/10.1002/aisy.202000035 , and https://doi.org/10.1021/acsapm.0c00626 - research articles on 4D printing by DLW
- https://doi.org/10.3390/micro1020013 - article about DLW on the Nanoscribe.

**Methods**

Materials - please add the product codes wherever possible, and include the purity of the chemicals. Please include all chemicals employed throughout the work (e.g. $HNO_3$, HCl, isopropanol, chloroform, copper tape are all missing).

Fabrication of ITO IDE - Please add details on the equipment employed (spin coater, hotplate) and correct the repeated use of the word "washed".

DLW of LCE structures - “The calculated amount of photoinitiator to achieve 7%mol. was dissolved in 0.5 mL of chloroform” – please include the actual value in addition to this text. "(...) a mixture of LC-DA and LC-MA" - please list the ratios employed for preparing the various LC mixtures. There is a typo in "Calmar laser source". What is the model of Photonic Professional system? Is it a GT2? Finally and most importantly, I believe that the DeScribe files (data, job, recipe etc) need to be included in the Extended data, in addition to the .stl files which are already included.

Evaluation of actuation properties - “Peltri plate” – do the authors mean Peltier element? "repeatedly heated up to 70 °C and cooled down to room temperature" - please include the number of heating / cooling cycles? "Measurements were taken using the image processing software of the instrument." - please provide the name and version of the software.

Simulations - in my opinion, the first paragraph of this section, with the exception of its first sentence, belongs in the Results and discussion section, rather than in the Methods section. How were the various parameters chosen? The authors mention is several places that xx is (...), "which we set to" yy (see $Q_n$ , $T_{ni}$ ). Similarly, "The LCE is modelled as a Linear Elastic Material with Young's Modulus E = 1 MPa, Poisson’s ratio ν ~ 0.5 (nearly incompressible), and density ρ = 1.2 g/cm$^3$." - how were the values chosen? Could the authors explain their choice or provide suitable references?

**Results and discussion**

The caption for Figure 1b is extremely confusing. There is no clear separation between the description of b) and the combined description of c) and d). I suggest rewriting as "**a**) Molecular structures of the liquid crystal elastomers (LCE) monomers employed. **b**) Indium-tin oxide (ITO) interdigitated electrodes: view of substrate. (**c,d**) Optical microscopy image of liquid crystals on substrate under cross polarizers, no bias applied (**c**) and with bias applied (**d**). **e**) Simulation of the distribution of the electric field generated by flat electrode, view along the plane (cross section)."

When discussing the LC formulation, the authors selected "the formulation comprising a 7:3 LC-MA:LC-DA mixture" as optimal. First of all, could the reasoning behind this choice be described in more detail. Secondly, the authors then refer to the "6:4 LC-MA:LC-DA" mixture as having "an excess of the difunctional LC", although the LC-DA is only 40% of the mixture. Could the authors reconsider the way they refer to the mixtures that have different ratios that the one deemed optimal?

In Figure 2 - please include **a)** and **b)** in the caption, since the images list this.

In the caption of Figures 2-5 - please include **a)**, **b)**, **c)** etc before the corresponding text description, in a similar manner to the caption of Figure 1.

In Figure 4a and Figure 5a, is it possible to provide images with higher magnification, or at least to crop the outer black area? It is rather difficult to observe anything in the current panels.

As the authors mention, the alignment observed in the structures is sub-optimal. When addressing potential reasons, the authors do not mention the fact that an electric field induces a rather transient alignment, which might be lost during the DLW process. What is the fabrication time for the various structures? Have the authors investigated for how long after applying the electrical current do the mesogens stay aligned? The Methods section mentions that "The samples were then rapidly transferred to a Photonic Professional system" (after performing the alignment using the horizontal electric field). I believe that thoroughly characterizing the ability of the system to maintain its alignment over time, after the voltage source is removed, would be extremely beneficial, as the system could well lose its alignment over (relatively short) periods of time.

Regarding the simulations and experiments: the heating / cooling cycles were 70C / 25C in the experiments, but 80C / 40C. Why is that? Would it not be more beneficial to employ the same temperature? In the Methods section, the authors mention that "$T_{ni}$ is the nematic-to-isotropic transition temperature, which we set to 60°C". Why was this value chosen, and was it confirmed experimentally as well?

**Conclusions**

This sections should be expanded. Since this is a Methods article, I believe the Conclusions section could briefly reiterate the process flow and emphasise crucial steps.

**References**

1. Bunea A, Martella D, Nocentini S, Parmeggiani C, et al.: Light-Powered Microrobots: Challenges and Opportunities for Hard and Soft Responsive Microswimmers. *Advanced Intelligent Systems*. 2021; **3** (4). Publisher Full Text
2. Nocentini S, Martella D, Parmeggiani C, Wiersma D: 3D Printed Photoresponsive Materials for Photonics. *Advanced Optical Materials*. 2019; **7** (16). Publisher Full Text
3. Nishiguchi A, Zhang H, Schweizerhof S, Schulte MF, et al.: 4D Printing of a Light-Driven Soft Actuator with Programmed Printing Density.*ACS Appl Mater Interfaces*. 2020; **12** (10): 12176-12185 PubMed Abstract | Publisher Full Text
4. De Bellis I, Ni B, Martella D, Parmeggiani C, et al.: Color Modulation inMorpho Butterfly Wings Using Liquid Crystalline Elastomers. *Advanced Intelligent Systems*. 2020; **2** (9). Publisher Full Text
5. Delaney C, Geoghegan N, Ibrahim H, O'Loughlin M, et al.: Direct Laser Writing to Generate Molds for Polymer Nanopillar Replication. *ACS Applied Polymer Materials*. 2020; **2** (8): 3632-3641 Publisher Full Text
6. Bunea A, del Castillo Iniesta N, Droumpali A, Wetzel A, et al.: Micro 3D Printing by Two-Photon Polymerization: Configurations and Parameters for the Nanoscribe System. *Micro*. 2021; **1** (2): 164-180 Publisher Full Text

**Is the rationale for developing the new method (or application) clearly explained?**

Partly

**Is the description of the method technically sound?**

Partly

**Are sufficient details provided to allow replication of the method development and its use by others?**

No

**If any results are presented, are all the source data underlying the results available to ensure full reproducibility?**
No

**Are the conclusions about the method and its performance adequately supported by the findings presented in the article?**
Partly

***Competing Interests:*** No competing interests were disclosed.

***Reviewer Expertise:*** Two-photon polymerization direct laser writing.

**I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.**

Author Response 16 Nov 2021

**Virgilio Mattoli**

**REPLY TO REVIEWER 1 COMMENTS** (Reviewer comments in italics)
*The article from Carlotti et al. describes the direct laser writing (DLW) of liquid crystal elastomer (LCE) microactuators which exhibit a reversible shape change of <10 % when actuated using heating (70C) / cooling (25C) cycles. The authors employed static electric fields to align the LCE mesogens before the DLW process and performed simulations to understand and verify their experimental results. DLW of LCE has been explored by various groups, so the novelty of the work is not very high, but it is reasonable for a Methods article. However, the experimental procedures are not described in sufficient details, especially for a Methods paper, and some of the data necessary to reproduce this work is missing. Furthermore, the introduction of the work is rather short, slightly misleading at times, and is missing some important articles from literature. I believe the article by Carlotti et al. is overall reasonably interesting and could be useful to the LCE DLW community. My detailed suggestions for improvement are listed below.*
**Author Reply:** We thank the reviewers for the time dedicated to our work. We incorporated their suggestions when it was possible and we hope that in this way the quality of the manuscript has improved. Below we address all the points raised.

*Introduction I believe that the introduction talks too much about MEMS and not enough about other relevant aspects, especially given the fact that the fabricated microactuators have potential for MEMS, but are not exactly MEMS by themselves. This is somewhat addressed in the Conclusions section. I suggest expanding the introduction to cover relevant aspect of DLW and reported applications of LCE patterned by DLW. Furthermore, I suggest mentioning that this paper is actually about 4D printing, since the fabricated structures are responsive to external stimuli. I suggest taking inspiration (and referencing) the following papers: https://doi.org/10.1002/aisy.202000256 and https://doi.org/10.1002/adom.201900156 - review papers covering microactuators prepared by LCE DLW. https://doi.org/10.1021/acsami.0c02781 ,*

*https://doi.org/10.1002/aisy.202000035 , and https://doi.org/10.1021/acsapm.0c00626 - research articles on 4D printing by DLW https://doi.org/10.3390/micro1020013 - article about DLW on the Nanoscribe.*
**Author Reply:** We thank the reviewer for the suggestions which was also raised by the second reviewer. We added several recent references to recent work and relevant reviews in version 2.

*Methods Materials - please add the product codes wherever possible, and include the purity of the chemicals. Please include all chemicals employed throughout the work (e.g. HNO3, HCl, isopropanol, chloroform, copper tape are all missing).*
**Author Reply:** Where possible we added such information.

*Fabrication of ITO IDE - Please add details on the equipment employed (spin coater, hotplate) and correct the repeated use of the word "washed".*
**Author Reply:** We added the missing information and fixed the repetition of the word ‘washed’.

*DLW of LCE structures - “The calculated amount of photoinitiator to achieve 7%mol. was dissolved in 0.5 mL of chloroform” – please include the actual value in addition to this text."(...) a mixture of LC-DA and LC-MA" - please list the ratios employed for preparing the various LC mixtures.*
**Author Reply:** Molar values were used as we did not always prepare the same amount of photoresist. However, we included an example recipe for those who are not familiar with the use of molar quantities.

*There is a typo in "Calmar laser source".*
**Author Reply:** We removed this specification, since it is related to the previous version of the system.

*What is the model of Photonic Professional system? Is it a GT2? Finally and most importantly, I believe that the DeScribe files (data, job, recipe etc) need to be included in the Extended data, in addition to the .stl files which are already included.*
**Author Reply:** We updated the info about our Nanoscribe system, that is the galvo update of GT, equivalent to a GT2. We also added an example of DeScribe outputs (containing full parameters for slicing and writing jobs) to the Extended Data. While doing this, we noticed a typo in the manuscript concerning the hatching distance (which was actually 0.2 instead of 0.3 as we previously wrote) and discrepancies in the reported laser power.

*Evaluation of actuation properties - “Peltri plate” – do the authors mean Peltier element? "repeatedly heated up to 70 °C and cooled down to room temperature" - please include the number of heating / cooling cycles? "Measurements were taken using the image processing software of the instrument." - please provide the name and version of the software.*
**Author Reply:** We changed ‘plate’ to ‘element’ and added the rest of the information in the text.

*Simulations - in my opinion, the first paragraph of this section, with the exception of its first sentence, belongs in the Results and discussion section, rather than in the Methods section. How were the various parameters chosen? The authors mention is several places that xx is (...), "which*

*we set to" yy (see Qn , Tni ). Similarly, "The LCE is modelled as a Linear Elastic Material with Young's Modulus E = 1 MPa, Poisson's ratio ν ~ 0.5 (nearly incompressible), and density ρ = 1.2 g/cm3." - how were the values chosen? Could the authors explain their choice or provide suitable references?*
**Author Reply:** The first paragraph was added upon request of the editor to explain the reason why we used proprietary software for the simulations rather than an open source one. We do not think such statements are critical in the exposition of the methodology and therefore we prefer to place them in the methods section rather than in the discussion where they would unnecessary lengthen the part. The mechanical parameters and density values are intended as representative of this class of materials (chosen according to [S. Palagi, A. G. Mark, S. Y. Reigh, K. Melde, T. Qiu, H. Zeng, C. Parmeggiani, D. Martella, A. Sanchez-Castillo, N. Kapernaum, F. Giesselmann, D. S. Wiersma, E. Lauga, P. Fischer, Nat. Mater. 2016, 15, 647] – the reference has been added in the new version), and not necessarily accurate for the specific 3D-printed microstructures (for which accurate measurement of all properties was out of the scope of this work). We have chosen the transition-related parameters (Qn, Tni, gamma) to roughly match the behavior observed in our microstructures. Again, the simulations were not performed as a predictive tool, yet as a way to interpret the observed results and have an intuitive view of the shape-change behavior.

*Results and discussion The caption for Figure 1b is extremely confusing. There is no clear separation between the description of b) and the combined description of c) and d). I suggest rewriting as "a) Molecular structures of the liquid crystal elastomers (LCE) monomers employed. b) Indium-tin oxide (ITO) interdigitated electrodes: view of substrate. (c,d) Optical microscopy image of liquid crystals on substrate under cross polarizers, no bias applied (c) and with bias applied (d). e) Simulation of the distribution of the electric field generated by flat electrode, view along the plane (cross section)."*
**Author Reply:** To make it more clear, we rephrased the caption as "a) Molecular structures of the liquid crystal elastomers (LCE) monomers employed. b) Photograph of indium-tin oxide (ITO) interdigitated electrodes. c-d) Optical microscopy images of liquid crystals on substrate under cross polarizers no bias applied (c) and with bias applied (d). e) Simulation of the distribution of the electric field generated by flat electrode, view along the plane (cross section)."

*When discussing the LC formulation, the authors selected "the formulation comprising a 7:3 LC-MA:LC-DA mixture" as optimal. First of all, could the reasoning behind this choice be described in more detail. Secondly, the authors then refer to the "6:4 LC-MA:LC-DA" mixture as having "an excess of the difunctional LC", although the LC-DA is only 40% of the mixture. Could the authors reconsider the way they refer to the mixtures that have different ratios that the one deemed optimal?*
**Author Reply:** Following the advices of both reviewer 1 and 2, we rewrote the paragraph as "We tried several different compositions and found that the formulation comprising a molar ratio of 7:3 LC-MA:LC-DA gave the best results for our scope. In particular, when compared to different mixtures, the printed structures showed an appreciable resolution (Figure 2) and resulted soft enough to observe the actuation (as discussed later and depicted in Figure 4). Increasing the amount of monoacrylate compound (8:2 LC-MA:LC-DA) resulted in structures that looked softer and less defined (see Figure 2), while increase of the quantity

of difunctional LC (6:4 LC-MA:LC-DA) gave rise to more rigid structures that did not actuate appreciably."

*In Figure 2 - please include a) and b) in the caption, since the images list this.*
**Author Reply:** Added.

*In the caption of Figures 2-5 - please include a), b), c) etc before the corresponding text description, in a similar manner to the caption of Figure 1.*
**Author Reply:** Done.

*In Figure 4a and Figure 5a, is it possible to provide images with higher magnification, or at least to crop the outer black area? It is rather difficult to observe anything in the current panels.*
**Author Reply:** We followed the suggestion of the reviewer to make the picture more pleasant and we cropped part of the black area.

*As the authors mention, the alignment observed in the structures is sub-optimal. When addressing potential reasons, the authors do not mention the fact that an electric field induces a rather transient alignment, which might be lost during the DLW process. What is the fabrication time for the various structures? Have the authors investigated for how long after applying the electrical current do the mesogens stay aligned? The Methods section mentions that "The samples were then rapidly transferred to a Photonic Professional system" (after performing the alignment using the horizontal electric field). I believe that thoroughly characterizing the ability of the system to maintain its alignment over time, after the voltage source is removed, would be extremely beneficial, as the system could well lose its alignment over (relatively short) periods of time.*
**Author Reply:** We understand the concerns of the reviewer and indeed we did not perform such investigation on our system. While we do not know for certain the evolution of the orientation with time, because of the solid nature of the resist, we are confident that the alignment is retained for at least hours so to allow the printing process. Unfortunately, at the moment we won't be able to perform such experiments anytime soon. We plan, however, to include this analysis in our follow up work on this subject.

*Regarding the simulations and experiments: the heating / cooling cycles were 70C / 25C in the experiments, but 80C / 40C. Why is that? Would it not be more beneficial to employ the same temperature? In the Methods section, the authors mention that "Tni is the nematic-to-isotropic transition temperature, which we set to 60°C". Why was this value chosen, and was it confirmed experimentally as well?*
**Author Reply:** While the simulations for the distribution of the electric field are helpful to explain the performances of flat electrodes, those concerning the response of LCEs are intended as support to clarify the expected actuation to readers not familiar with such materials. In this sense, they do not represent a full description of the system involved. In general, when such calculations are performed, they do not entail any molecular or atomistic details and thus the characteristic parameters (such as transition temperature, young modulus, and ordering) are external inputs. The 80/40 interval was set to represent the full deformation range across the transition temperature. This was set to 60 C since experimentally we noticed that the actuation started at around 50 C (both in the thin film and DLW printed structures) and was complete at 70 C as we mention in the text. For this

reason, the interval of interest for the temperature response in simulations was chosen to be between 40C and 80C, which includes the one observed experimentally.

*Conclusions This sections should be expanded. Since this is a Methods article, I believe the Conclusions section could briefly reiterate the process flow and emphasise crucial steps.*
**Author Reply:** Such part was added as we agree that makes the article more effective for the readers.

***Competing Interests:*** No competing interests were disclosed.