Tuning Cholesteric Selective Reflection In Situ Upon Two-Photon Polymerization Enables Structural Multicolor 4D Microfabrication

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Effective optical elements with tailored properties often rely on the capability to tune the material’s structure at the nanoscale. Thanks to their self-organized 1D helical arrangement, cholesteric liquid crystals represent a beautiful example of optical materials whose properties are governed by their supramolecular structure. According to the Bragg’s law, selective reflection of circular polarized light occurs for wavelengths within the photonic band gap, which, beside the refractive indices, depends on the helix pitch. Here, polymeric microstructures with tailored PBG are demonstrated by two-photon polymerization direct laser writing in cholesteric reactive mesogens. Turning a renowned disadvantage into an opportunity, the shrinkage upon the layer-by-layer photopolymerization is exploited to control the effective helix pitch. Starting from a PBG of the precursor in the near infra-red, micro-cylinders which exhibit Bragg selective reflection at lower wavelength ranges, down to the opposite end of the visible spectrum, are fabricated in a single-step process by tuning the laser exposure parameters. As a proof-of-concept, a 4D quick response (QR) micro-tag, which adds the polarization-selective structural color and the height of the blocks to the usual 2D black/white QR codes, is demonstrated as a novel paradigm of optical anti-counterfeiting microdevice.

1. Introduction

In the last decades, micro- and nano-additive manufacturing has been of great interest, both in scientific and technological fields, due to the possibility to fabricate systems and devices featuring micrometer and nanometer resolution.[1–3] Among the different technologies, two-photon direct laser writing (DLW) is nowadays one of the best techniques to pattern metallic nanoparticles in complex geometry[4–11] and to nano-fabricate polymeric 3D structures.[12–21] Briefly, a near infra-red (NIR) ultrafast laser, with high peak power, is tightly focused inside a UV-sensitive photoresist to promote highly localized photochemical reactions through the simultaneous absorption of two (or more) photons. As a third-order non-linear optical process, two-photon absorption (TPA) cross-section depends on the square of the intensity of the laser beam. The polymerization of the liquid-phase precursor is a threshold phenomenon which occurs within the focus figure, inside a sub-micrometric prolate spheroid which defines the smallest printable volume (i.e., voxel). By precisely sweeping the laser focus along the designated path, line by line, 3D microstructures of photocured material are created.

Liquid crystals (LCs) have demonstrated a periodically re-emerging interest ever since the added value of innovation was introduced when combined with new materials and/or technologies due to their flexibility to self-organize in ordered structures at different scales[22–28] and their sensitivity to external stimuli.[29–38] In the field of additive manufacturing by two-photon polymerization (TPP) DLW, the use of mixtures of photopolymers and low molar mass LCs as well as photopolymerizable LCs, also known as reactive mesogens (RMs), paved the way for 3D custom soft photonic devices with tunable properties[39–44] and new solutions for micro-robotics.[45–51] LC elastomers have been employed to fabricate micro-robotic structures, with desired shapes and dimensions, maintaining designed molecular orientation, which can perform reversible shape modification controlled by light.[52–56] TPP-DLW on LCs and monomer mixtures enabled to create electrically controllable complex, multi-dimensional micron-scale structures (i.e., scaffolds) with tunable optical properties.[57–59]

However, a thorough investigation on the effect of TPP-DLW on the intrinsic properties of the RMs, and on the possibility to deliberately alter them locally in the solidified phase...
is still missing. In particular, the potential to fabricate 3D microstructures in materials whose linear and circular optical anisotropies could be tuned with high spatial resolution in a single-step during the DLW process could lead toward innovative photonic devices, such as micro-lasers, white light reflective micro-objects, and anti-counterfeiting elements.

Among the different LC phases, the cholesteric (i.e., chiral nematic) one is characterized by a spontaneous 1D periodic structuration at the nano/micrometric scale, which determines its distinguishing optical properties. The helical supramolecular arrangement (Figure 1a) affects the density of photon states, and a photonic band gap (PBG) is established. Photons with the same helicity as the cholesteric arrangement and wavelengths comparable to the helix pitch undergo selective reflection when they propagate close to the axis of the cholesteric.[60–64] Based on these features and on their tuning strategies via external stimuli, cholesterics have been largely investigated for photonic and optical applications.[65–73] Cholesteric RMs (CRMs) as well as polymer stabilized cholesteric LCs have demonstrated to improve photonic[74,75] and optomechanic[76,77] performances on cholesteric based devices by freezing the supramolecular chiral structures.

In this work, we harness the TPP-DLW on CRMs to demonstrate a wide tunability of the helix pitch in polymerized microstructures, which can be achieved at the microscale during the manufacturing procedure. The capability to alter locally the optical properties of the photocured polymer (i.e., the PBG of the CRMs), independently from the shape and size of the 3D object, effectively adds a fourth dimension to the TPP-DLW technique. First, polymer microcylinders which exhibit selective Bragg reflection for different wavelength ranges across the whole visible spectrum are manufactured in a single CRMs mixture and fabrication session. Sharing the same computer-aided design (CAD) model, the objects only differ for the irradiation parameters, that is, laser power (LP) and scan speed (SS), which thus allow for the effective PBG tuning. As a simple explanation of the phenomenon, one can think of the inhomogeneous polymerization degree which occurs in the layer-by-layer fabrication process. The shrinking of the microstructure after development preferentially occurs in the direction of the polymerization gradient and is proposed to account for the reduction of helix pitch with respect to the LC phase. Second, in view of the potential application impact of single-step microfabrication of 3D objects with spatially resolved structural colors, a 4D quick response (QR) code is reported as a new paradigm of high-security anticounterfeiting micro-tag, classifiable as a quasi-strong physically unclonable function (PUF).[78] The 4D-QR tag, fabricated in the same CRMs mixture over a 100 × 100 µm² area, is made of 25 × 25 micron-sized square cuboid elements, with different heights and selective reflection color bands. Providing two further dimensions with respect to the standard black/white 2D QR, it can encode much larger amount of information; it allows for increasing levels of complexity and security in the optical and topographic read-out processes, is virtually unclonable.

2. Tuning Cholesteric Bragg Reflection by Direct Laser Writing

In TPP-DLW lithography, a CAD model of the 3D structure is usually sliced in layers and each layer is filled with horizontal lines (hatching) which form the writing path of a tightly focused ultrafast NIR laser. To obtain compact solid structures, slicing and hatching values must be adjusted according to the voxel height and width respectively, which in turn depend on the delivered energy dose.[79] When DLW is applied to RMs, it is usually desirable that the laser exposure does not perturb the orientational order of the LC phase, so that photocured polymer preserves the local birefringence and director orientation. To this aim, calibration of the TPP-DLW fabrication process has been preliminarily carried out in the nematic RMs mixture (see Supporting Information). In CRMs, the director is not uniform, because molecules spontaneously self-assemble into a helical superstructure (Figure 1a) which grants the circular-polarization selective Bragg reflection at normal incidence in a wavelength range centered at , where is the average refractive index and the helix pitch.[60–62] When single-photon absorption process is exploited, even in the case of tightly focused UV beams (Figure 1b), photoactivation is not confined to a specific plane into the photoresist, and polymerization simultaneously occurs over distances much larger than the helix pitch.[80] In this case, the whole helical structure is frozen and the PBG of the polymer replicates that of the LC phase, possibly slightly blue-shifted because of the homogeneous shrinkage.[81]

On the other hand, the highly localized polymerization which occurs in TPP-DLW allows for inhomogeneous and anisotropic shrinking.[82] Indeed, in the near-threshold exposure condition, the voxel dimensions can be much smaller than the CRMs pitch, and only a fraction of the helix is fully

Figure 1. a) Scheme of the helical order of the CRMs infiltrated inside a cell, induced by planar aligning rubbed polyvinyl alcohol (PVA) films. b) The UV light triggers the cross-linking of the monomers in a volume (in light blue) whose linear dimension is typically larger than the CLCs pitch. The resulting polymer structure preserves the CLCs architecture, with a limited shrinkage. c) In the TPP-DLW, the NIR focused beam (in pink) leads to the polymerization of the UV-sensitive CRMs only in a sub-micrometric voxel (in light blue), whose height could be shorter than the pitch.
photopolymerized (Figure 1c). If overlap between neighboring voxels is limited, inhomogeneous polymerization occurs that, although sufficient to guarantee the consistence of the microstructure, causes greater shrinkage of the structure after development. In CRMs, this process can be exploited to adjust the effective pitch of the helical superstructure, thus inducing a controlled blue-shift in the selective Bragg reflection.

The CRMs are obtained here by doping a commercial acrylate-based nematic RMs mixture (Licrivue RMS03-001C by Merck, see Figure S1, Supporting Information) with a left-handed chiral component (S811, Merck), to achieve the desired helix pitch (see Experimental Section). When confined between two parallel substrates that promote homogeneous (planar) molecular alignment, the director lies parallel to the substrates and the spontaneous cholesteric organization occurs with the helical axis perpendicular to them. The effect of the shrinkage on the PBG of the CRMs upon polymerization was preliminarily evaluated by exposing the films to UV light (0.23 mW cm\(^{-2}\) @ \(\lambda_{\text{max}}\) = 365 nm, exposure time = 1 h), for three chiral dopant concentrations, namely 17%, 19%, and 20% by weight (see Figure S3, Supporting Information). The blue-shift of the PBG’s central wavelength upon uniform single-photon polymerization is limited to \(\approx 20\) nm in the NIR, namely from 810 to 790 nm, at the lower (i.e., 17%) S811 concentration, and \(\approx 10\) nm in the visible spectrum for the 19% and 20% S811 concentrations (see Table 1). A significantly larger effect, with blue-shifts of the order of 100 nm, can be achieved when TPP-DLW is exploited, even for simple solid figures. Micron-sized cylinders are manufactured in the CRMs, for the three chiral dopant concentrations mentioned above, starting from a CAD model with diameter \(d = 50\) µm and height \(h = 10\) µm, sliced in planes parallel to the cell’s substrates (see Experimental Section). The polymeric structures, fabricated with LP = 175 mW and SS = 4.0 mm s\(^{-1}\), reproduce the shape and the transverse size of the model (i.e., the diameter of the cylinder), as shown by atomic force microscope (AFM) imaging (Figure 2a), although, with an average height of 7.9 µm, they are shorter. Optical imaging of the same cylinders, carried out in reflection mode, makes evidence of their selective reflection bands, which span the visible range: red (Figure 2b), green (Figure 2c), and blue (Figure 2d), for the CRMs at 17%, 19%, and 20% S811 concentration, respectively. Spectral characterization of the TPP-DLW

![Figure 2](image_url)

**Figure 2.** a) AFM imaging of a polymeric structure microfabricated by TPP-DLW in CRMs from a cylindrical CAD model (diameter: 50 µm, height: 10 µm, slicing: 0.4 µm, hatching: 0.3 µm) at LP: 17.5 mW and SS: 4.0 mm s\(^{-1}\). The average height of the structure is 7.9 µm, which corresponds to a relative shrinking after development of \(\approx 21\)%.

**Table 1.** Central wavelengths obtained by spectrophotometry of three samples of RMS doped with three different concentrations of S811, taken before and after photo-polymerization. While the blue-shift induced by the single-photon polymerization is in the order of 10 nm, the TPP-DLW process generates a consistent blue-shift of \(\approx 150\) nm in all the analyzed cases, for the cylinders made at LP = 17.5 mW and SS = 4.0 mm s\(^{-1}\).

| Concentration | Before polymerization | After UV-polymerization | After TPP-DLW |
|---------------|-----------------------|-------------------------|--------------|
| 17%           | 810 nm                | 790 nm                  | 640 nm       |
| 19%           | 670 nm                | 660 nm                  | 520 nm       |
| 20%           | 620 nm                | 610 nm                  | 480 nm       |
polymeric structures (see Experimental Section) confirms the considerable shift of the PBGs, whose central wavelengths (Table 1) are from 140 to 170 nm lower than the unpolymerized CRMs ones. AFM analysis of cross-section of the polymeric cylinders (see Figure S4, Supporting Information) proves the corresponding reduction of the cholesteric pitch upon TPP-DLW, which well correlates with the shift of the PBG. Remarkably, the relative blue-shifts of the PBGs (22%), as well as the 2.1 \( \mu \)m vertical shrinking (i.e., 21% relative shrinking), are similar for all the microcylinders fabricated in the different CRMs. Both are influenced by the average degree of polymerization, which in turn depends on the CAD model (i.e., shape, sizes, slicing, and hatching) and the TPP-DLW parameters (i.e., LP and SS). When the voxel height matches or slightly exceeds the slicing value, which is here comparable to the helix pitch \( p \) of the CRMs (left columns), almost homogeneous polymerization occurs. The shrinking of the polymeric structure after development (on the right side) is minimized and, therefore, the actual pitch \( p_e' \leq p \). When the voxel height is shorter than \( p \) and the slicing distance (right columns), inhomogeneous polymerization takes place. Upon development, a large fraction of unpolymerized CRMs is washed out, which results in an enhanced shrinkage of the structure, that is, \( p_e'' < p_e' \). Reflection mode microscope imaging of a cylindrical structure fabricated at LP = 15 mW and SS = 8.0 mm s\(^{-1}\) in the CRMs at 17% of S811, b) before and c–f) after the development. The photocured structure is barely visible when surrounded by the unpolymerized CRMs, both showing a PBG centered in the NIR (b). Immediately (< 1 min) after the specimen is removed from the development bath, the microcylinder already exhibits a shift of the PBG, with a red selective reflection centered at 650 nm (c). As the solvent evaporates and the polymerized structure shrinks, the PBG blue shifts to orange (after 30 min), yellow (after 1 h), and finally stabilizes to cyan (after 24 h).

Figure 3. The control of the voxel size in TPP-DLW allows for fine tuning the effective helix pitch. a) Setting both the slicing and voxel height close to the helix pitch \( p \) of the CRMs (left columns), almost homogeneous polymerization occurs. The shrinking of the polymeric structure after development (on the right side) is minimized and, therefore, the actual pitch \( p_e' \leq p \). When the voxel height is shorter than \( p \) and the slicing distance (right columns), inhomogeneous polymerization takes place. Upon development, a large fraction of unpolymerized CRMs is washed out, which results in an enhanced shrinkage of the structure, that is, \( p_e'' < p_e' \). Reflection mode microscope imaging of a cylindrical structure fabricated at LP = 15 mW and SS = 8.0 mm s\(^{-1}\) in the CRMs at 17% of S811, b) before and c–f) after the development. The photocured structure is barely visible when surrounded by the unpolymerized CRMs, both showing a PBG centered in the NIR (b). Immediately (< 1 min) after the specimen is removed from the development bath, the microcylinder already exhibits a shift of the PBG, with a red selective reflection centered at 650 nm (c). As the solvent evaporates and the polymerized structure shrinks, the PBG blue shifts to orange (after 30 min), yellow (after 1 h), and finally stabilizes to cyan (after 24 h).
are observed in the next days/weeks/months (up to 1 year), in the temperature range 4–90 °C. Such further 170 nm blue-shift with respect to the as-developed specimen of Figure 3c is likely related to the solvent evaporation and consequent deswelling of the structure. The overall 330 nm shift in the PBG of the dry structure with respect to the precursor CRMs one is much larger than that reported in Figure 2b and Table 1, for the same 17% S811 concentration but different TPP-DLW parameters. It can be rationalized in term of the lower degree of polymerization resulting from the lower LP and higher SS, which causes larger shrinking of the polymerized structure and lower effective helix pitch (see Figure 3a, where $p_e'' < p_e'$). This hypothesis is confirmed by the actual height of the cylinder, 6.0 µm as measured by AFM, which is 24% shorter than the 79 µm-tall cylinders printed at LP = 17.5 mW and SS = 4.0 mm s$^{-1}$ (see Figure 2a). Within the experimental error, it correlates remarkably well with the 25% relative difference between the PBG’s central wavelengths of the structures in Figure 2b (640 nm) and Figure 3f (480 nm).

Controlling the effective helix pitch via the anisotropic shrinking, TPP-DLW allows to move the PBG of CRMs from the NIR to both edges of the visible spectrum. The next step forward is to tune it all the way through the spectral range of interest. This would enable to manufacture 3D objects exhibiting multiple structural colors, in a single CRMs mixture and TPP-DLW session, by simply adjusting the writing parameters. Figure 4a reports the microscope image of a $3 \times 4$ matrix of isolated structures fabricated from the same cylindrical CAD model, by varying the LP and SS values in the range 12.5–17.5 mW and 4.0–10 mm s$^{-1}$, respectively. The circularly polarized light reflected by the polymerized cholesteric cylinders spans the visible spectrum, from red to violet. The blue shift of the PBG increases as the LP decreases and/or the SS increases, from the bottom to the top and from the left to the right side of the matrix, respectively. Spectrophotometric analysis of the reflected light is carried out on each structure of the matrix. Selected spectra (Figure 4b) and the peak intensity wavelengths (Figure 4c) of the PBGs are reported versus LP and SS. The PBGs, with a FWHM bandwidth of ≈100 nm, span the whole visible spectral range, from 650 to 385 nm, with comparable peak intensity. Only in the deep violet range, below 420 nm, the intensity of reflected light significantly falls (see the purple curve, for LP = 12.5 mW and SS = 6.0 mm s$^{-1}$, in Figure 4b), which confirms the evident brightness reduction in the top row of Figure 4a. Indeed, AFM imaging evidences a truncated cone shape of the structures exposed at LP = 12.5 mW, proving a larger deviation from the CAD model, in both shape and height, with respect to the ones exposed at higher LP. Furthermore, at LP = 12.5 mW and SS ≥ 8.0 mm s$^{-1}$, the structures become heavily underexposed, characterized by irregular shapes and a sudden drop in height (from 3.5 to 0.7 µm for SS = 6.0 and 8.0 mm s$^{-1}$, respectively), or virtually absent at SS = 10 mm s$^{-1}$.

3. 4D Quick Response Tag

The reported results are of great relevance from a technological point of view in the fields of miniaturized optics, lasers, and anti-counterfeiting. In this regard, a new paradigm of sophisticated secure authentication code is proposed here, by extending the 2D QR code. Exploiting the tunability of the PBG demonstrated here, in conjunction with its intrinsic 3D fabrication capability, the TPP-DLW in CRMs would not only allow to add a third dimension (i.e., height) to a micron-sized QR, but also to introduce a structural, polarization selective, color
code. The resulting micro-tag would be a hardly falsifiable 4D QR secure system, which can potentially store a significant amount of data and can be readout at increasing level of complexity, by the end users (e.g., with laser scanner and/or mobile phone cameras) up to the forensic level (with polarizing microscope, profilometer and/or AFM). As a proof test, the $25 \times 25$ QR code in Figure 5a (which points to the website of the University of Calabria, http://www.unical.it), has been uniformly “extruded” in a $100 \times 100 \times 5.2 \ \mu m^3$ 3D CAD model. By separately hatching each square cuboid “pixel”, all can be potentially printed with different TPP-DLW parameters (i.e., LP and SS) in order to confer them unique PBG central wavelengths. Here, the 625 “pixels” of the QR code have been sorted in four groups (Figure 5b), sharing the LP ($15 \ \text{mW}$) but differing for the SS (from 4.0 to $7.0 \ \text{mm s}^{-1}$) and manufactured in the CRMs at 17% of S811. The exposure time of the entire QR code is less than 4 min ($\approx 220 \ \text{s}$). The AFM imaging of the QR tag is reported in Figure 5c. As expected, the polymeric structure exhibits a non-uniform height, which ranges from 3.2 to $4.0 \ \mu m$, because of the uneven shrinking due to the four SS values adopted in the pixel sectors of Figure 5b. The transmission bright field optical micrograph of the QR tag, carried out in unpolarized light, is reported in Figure 5d. Albeit the structure is clearly distinguishable, such imaging mode conceals the circularly polarized light selective reflection. On the other hand, the structural colors map across the QR tag is strikingly evident in cross-polarization reflection mode microscopy (see Figure 5e) and closely resembles the corresponding SS map of Figure 5b. Microspectroscopy analysis of the various sections of the QR tag has evidenced four groups of PBGs, whose central wavelength ranges from 490 nm, for the shortest cuboidal “pixel”, to 600 nm, for the $4.0 \ \mu m$ high sectors. It is worth mentioning that the topographic and color maps of the QR tag reported here are directly correlated, since both are affected merely by the SS map in Figure 5b. Indeed, for the sake of simplicity, the CAD model has been created with the same height for the all the cuboid “pixels”. It is however straightforward to decouple the topographic profile of the QR tag from its polarization selective structural color map, if simply a 3D CAD model with multiple pixels heights is considered.

4. Conclusion

When TPP-DLW is applied to liquid crystalline photoresists, tuning their physical properties with spatial resolution has the potential to confer further dimensions to the standard 3D additive manufacturing technique. In this work, we report on the wide tunability of the selective Bragg reflection band of a single cholesteric resist upon TPP, whose central wavelength can be adjusted continuously in the visible range, from 650 to 385 nm. The tuning strategy relies on the laser exposure parameters, namely LP and/or SS, and allows for 2D color mapping with micron-scale resolution. As such, the combination of TPP-DLW
and CRMs has the potential to pave the way toward rapid, single-step, and low cost “true-colors 3D” (or 4D) microfabrication, with relevant scientific and technological outcomes in the fields of miniaturized optics and photonics.

The underlying mechanism is ascribed to the inhomogeneous photopolymerization, which is to some extent intrinsic to the line-by-line TPP-DLW technique and is here mastered by advisedly reducing the voxel size. The consequent anisotropic shrinking of the polymeric structures upon development, thanks to the crisscrossed hatching of consecutive layers, preferentially occurs along the cholesteric helix axis and determines a corresponding compression of the effective helix pitch. The latter correlates exceptionally well with the blue-shift of the native NIR PBG of the unpolymerized CRMs.

In order to proof test the capability of the technique, a four-colors, polarization selective, 4D QR microtag is reported here, whose complete readout requires multiple physical approaches (polarizing optical imaging, microspectroscopy, and topographic mapping), and which represents a first example of a new concept of high-security 4D authentication code for anti-counterfeiting applications.

5. Experimental Section

Substrates and Cells: A thin (~20 nm) polyvinyl alcohol (PVA, 98% hydrolyzed, molecular weight: 13 000–23 000 g mol⁻¹, Aldrich) film was layered on glass coverslips (22 × 22 × 0.13 mm³) by spin coating of a PVA aqueous solution (3% by weight) at 3600 rpm and baked at 105 °C for 40 min. After slow cooling to room temperature, the PVA films were bidirectionally rubbed with a velvet roll to promote homogenous planar anchoring of the RMs.[31] Cells were assembled by gluing two coverslips with the rubbed PVA films facing each other parallelly, separated by 12-μm-thick Mylar spacers, using a UV-curing adhesive (Norland Optical Adhesive 65).

Reactive Mesogens: A commercial nematic RMs mixture was used here (Liciruvec RMS03-001C, Merck), which consists of four mesogens (mono- and diacrylates, see Figure S1, Supporting Information) dissolved in propylene glycol monomethyl ether acetate (PGMEA).[32] The solution was left for 24 h at 50 °C in a vacuum chamber (0.3 × 10⁻³ mbar) to allow for complete evaporation of the solvent. The unpolymerized nematic RMs mixture exhibits a clearing point at 75 °C. Upon UV irradiation (or TPA), the photoinitiators decompose into free radicals, starting a chain reaction of the reactive acrylate tails, which results in the creation of a cross-linked network of carbon–carbon bonds. The ordinary and extraordinary refractive indices of the cured material are \( n_o = 1.529 \pm 0.005 \) and \( n_e = 1.684 \pm 0.005 \) (at 20 °C and 589 nm). To increase the two-photon absorption cross-section of the RMs and promote cross-linking in the TPP-DLW fabrication, the photo-initiator phenylbis(2,4,6-trimethylbenzoyl)-phosphine oxide (Irgacure 2100) was added to the residue, 3% by weight, and the mixture was stirred for 1 h at 60 °C. The cholesteric phase (i.e., the CRMs) was obtained by doping the nematic RMs mixture with a left-handed chiral component (SB11, Merck). Three different concentrations, namely 17%, 19%, and 20% by weight, were used which yielded PBGs of the unpolymerized mixtures with central wavelength at \( \lambda \approx 810, 670, \) and 620 nm, and helix pitches \( p = \lambda / \pi \approx 505, 420, \) and 385 nm, respectively. CRMs were infiltrated into the cells by capillary force, in the isotropic phase and slowly cooled down in the cholesteric phase. Given the planar anchoring, the CRMs self-organized with the helical axis perpendicular to the substrates.

Two-Photon Polymerization Direct Laser Writing: 3D objects were microfabricated by the commercial DLW workstation Photonic Professional GT (Nanoscribe GmbH). A linearly polarized erbium-doped fiber laser (central wavelength: 780 nm, pulse duration: 100 fs, repetition rate: 80 MHz) was coupled to an inverted microscope and focused on the sample through a 63×, 1.4 N.A. oil-immersion objective (Zeiss, Plan Apochromat). The computer-aided design (CAD) models of the 3D structures were sliced in layers, parallel to the cell substrates, every 0.5 μm (slicing) and each layer was filled with parallel lines, every 0.3 μm (hatching), which formed the writing path of the laser focus. Consecutive layers were hatched in orthogonal direction, since crisscrossed arrangement of polymeric ribbons confers lateral stability to the final structure. A piezotranslation stage was used to set the sample position with respect to the focal plane, starting the TPP-DLW process from the bottom substrate. In each slice, the laser focus was swept along the hatching lines by a galvo scanner at different SS and LP, in the range 4–10 mm s⁻¹ and 12.5–17.5 mW (measured before the objective), respectively. The exposure time of the microstructures was of the order of 1 and 4 min for the microcylinders (\( d = 50 \mu m, h = 10 \mu m \)) and the QR tag (\( l \times l \times h = 100 \times 100 \times 5.2 \mu m^3 \)), respectively. After the TPP-DLW process, the cells were bathed in PGMEA for 25 min to remove the unpolymerized CRMs and facilitate the mechanical detachment of the two substrates. The development of the 3D structures, attached to the bottom cells’ substrates, was completed by a further bath in PGMEA for 10 min and left to dry in air at room temperature for 24 h, unless differently stated, to allow for complete solvent evaporation.

Optical Microscopy and Spectrophotometry: Optical micrographs were acquired with a polarizing upright microscope (Zeiss Axio Scope A1) equipped with a halogen (HAL 100) or mercury (HXP 120) illuminator, 20× / 0.50 or 50× / 0.70 objective (Zeiss Epiplan POL) and a DSLR camera (Canon EOS 600D). Optical imaging was carried out in reflection mode, unless otherwise stated. The PBG of the CRMs cylinders was investigated by collecting the Bragg reflected light with a fiber-optic spectrophotometer (Avantes, AvaSpec 2048), coupled to the same upright polarizing microscope (Zeiss Axio Scope A1), equipped with the mercury illuminator and a 100× objective (Zeiss Epiplan-Neofluar 100x / 0.75 HD). Both the micrographs and the spectra were collected in reflection mode between crossed linear polarizers, in order to discriminate against the light reflected by the glass substrate.

Atomic Force Microscopy: Topographic imaging of the 3D structures and their cross-sections was carried out at ambient conditions with an atomic force microscope (Bioscope Catalyst, Bruker–Nano), operating in non-contact mode with a silicon tip (radius 8 nm) on an antimony (n) doped Si cantilever (model: RTESP-300, k = 40 N m⁻¹, resonant frequency \( f_0 = 300 \) kHz).

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.
Data Availability Statement

Research data are not shared.

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