

# Paintable Encapsulated Body-Temperature-Responsive Photonic Reflectors with Arbitrary Shapes

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# Paintable Encapsulated Body-Temperature-Responsive Photonic Reflectors with Arbitrary Shapes

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## Supporting Information

**ABSTRACT:** A temperature-responsive photonic coating on a flexible substrate was prepared by a photoinduced phase-separation process. In this coating a low molecular weight cholesteric liquid crystal (Ch-LC) mixture was encapsulated between the substrate and an *in situ* formed protective polymer top layer. The photonic coating showed a blue-shift of the photonic reflection band of 100 nm by heating from 22 to 23 °C due to the close proximity to the smectic to cholesteric phase transition and an overall 330 nm blue-shift while heating from 22 to 45 °C. Hence, the red coating turned green upon contact with skin within seconds. Furthermore, the coating structure and composition were investigated in detail, revealing a thick top coat. The adhesion of the coating was improved by providing trays on the substrate (by etching or 3D printing), resulting in a link between arbitrary-shaped substrates and the protective polymer top layer. These bendable coatings could be of interest for sensors, anticounterfeit labels, or customizable aesthetic applications.



**KEYWORDS:** temperature-responsive polymers, cholesteric liquid crystals, photonic materials, coatings, polymerization-induced phase separation

## INTRODUCTION

Cholesteric liquid crystal (Ch-LC) photonic materials that change color based on temperature variations are of great interest for responsive pigments, smart textile, optical sensors, and smart windows.<sup>1–7</sup> Commercially available, (disposable) optical Ch-LC thermometers have, for example, been developed for healthcare and other applications.<sup>8</sup> Because of the anisotropic nature of liquid crystals and the helical arrangement, Ch-LCs reflect light similarly to Bragg reflectors. Often low molecular weight Ch-LC mixtures are sandwiched between two glass plates or foils, creating a stimuli-responsive photonic cell.<sup>8–14</sup> The high mobility of the low molecular weight LC molecules enables large and fast reflection band shifts when exposed to environmental changes such as temperature variations. To create mechanically robust coatings, it is usually desirable to cross-link LCs, which usually comes at the expense of the amplitude and/or speed of the optical response.<sup>15</sup> Various approaches have been studied to overcome this restriction, including polymer dispersed LC films<sup>16,17</sup> and hydrogel-like<sup>18,19</sup> or elastomeric LC photonic coatings.<sup>20,21</sup>

Recently, we<sup>22</sup> and others<sup>23</sup> have reported on paintable temperature-responsive Ch-LC reflectors encapsulated in a single flexible polymer substrate. These polymer coatings consist of microscale polymer containers filled with a Ch-LC solution created by a two-stage polymerization-induced phase

separation method<sup>24</sup> using a mask. The reflectivity of coatings changed over a large temperature range.

In this report, we used phase-separated Ch-LC coatings to create fast temperature-responsive photonic coatings, which need only 1 °C temperature difference to experience a 100 nm blue-shift of their photonic reflection band. If one uses the difference between room temperature and skin temperature, a red to green shift occurred within seconds. Additionally, the phase separation of the coating was investigated in detail by comprehensive optical and confocal characterizations of the coating structure and composition, revealing a relatively thick top coating. Polymer substrates were also used that contained trays avoiding the use of a mask exposure step during the coating process. These trays could be created by 3D printing allowing to produce arbitrary-shaped patterned photonic coatings with enhanced adhesion and a highly sensitive temperature-responsive paint by using an easy-to-use one-stage bar-coating technique.

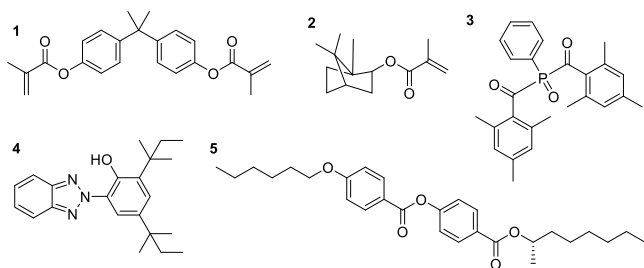
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## EXPERIMENTAL SECTION

**Materials.** The 500  $\mu\text{m}$  thick LEXAN 8040T film (made of polycarbonate) was kindly provided by SABIC. Etched PC substrates were purchased from Philips. Black (i.e., RAL 9005) poly(lactic acid) (PLA) filament was purchased from Ultimaker. Bisphenol A dimethacrylate (1), isobornyl methacrylate (2), and a LC mixture MLC-2138 and chiral dopant S811 (5) were purchased from Merck. Ciba IRGACURE 819 (3) and Ciba TINUVIN 328 (4) were purchased from Ciba Specialty Chemicals Ltd. The molecular structures are depicted in Figure 1.



**Figure 1.** Molecular structures of monomers used. The Ch-LC component of the mixture contains a mesogenic mixture MLC-2138, for which the molecular structures are unknown, and was doped with the chiral mesogen 5.

**Temperature-Responsive Paint (Ch-LC Mixture).** The mixture contains 4 wt % cross-linker (1), 45.5 wt % monoacrylate (2), 0.5 wt % photoinitiator (3), 0.3 wt % dye (4), 15 wt % chiral dopant (5), and 34.7 wt % MLC-2138.

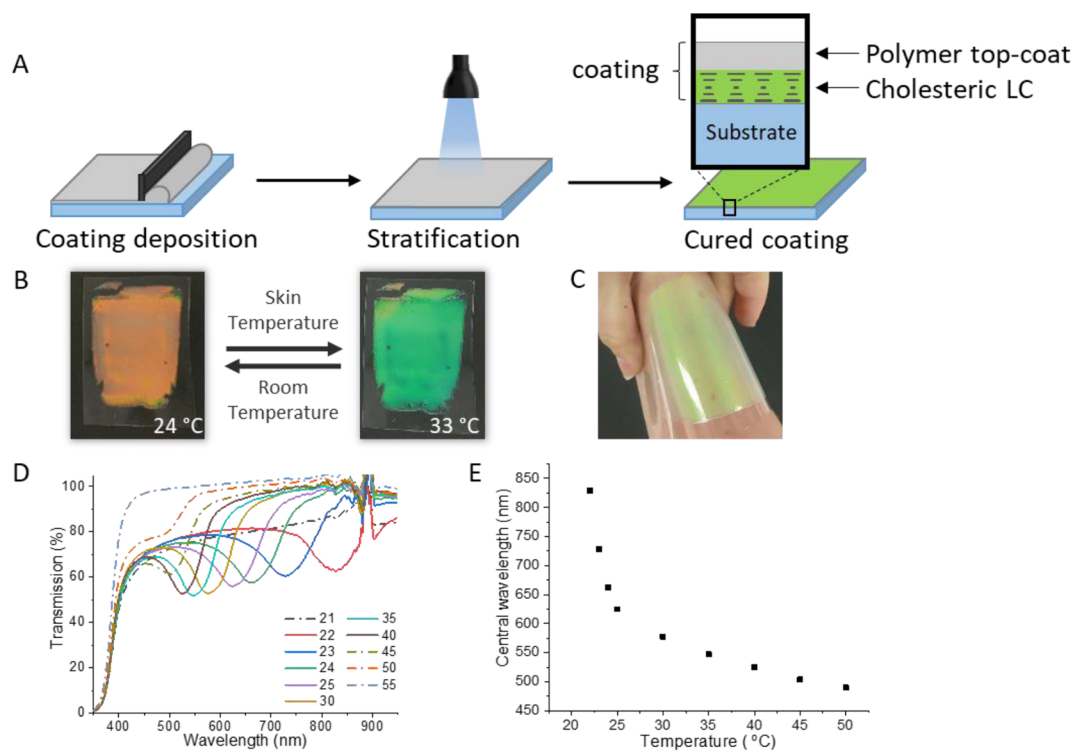
**Temperature-Responsive Coating Procedure.** The Ch-LC mixture was spread on a PC substrate by using an 80  $\mu\text{m}$  wire wound rod. The coating was cured in a nitrogen atmosphere at 42  $^{\circ}\text{C}$  by using 0.8  $\text{mW}/\text{cm}^2$  UV light (320–390 nm) for 20 min. The coatings were postcured with 30  $\text{mW}/\text{cm}^2$  UV light (320–390 nm) for 5 min.

**3D-Printed Substrates.** PLA substrates were printed by using an ultimaker 3 3D printer and black PLA filament. The substrates have a total thickness of 2 mm and an average layer height of 200  $\mu\text{m}$ . All layers except the final layer are completely filled with the polymer. In the final layer, only the veins and contour of the butterfly were printed (schematically shown in Figure S1).

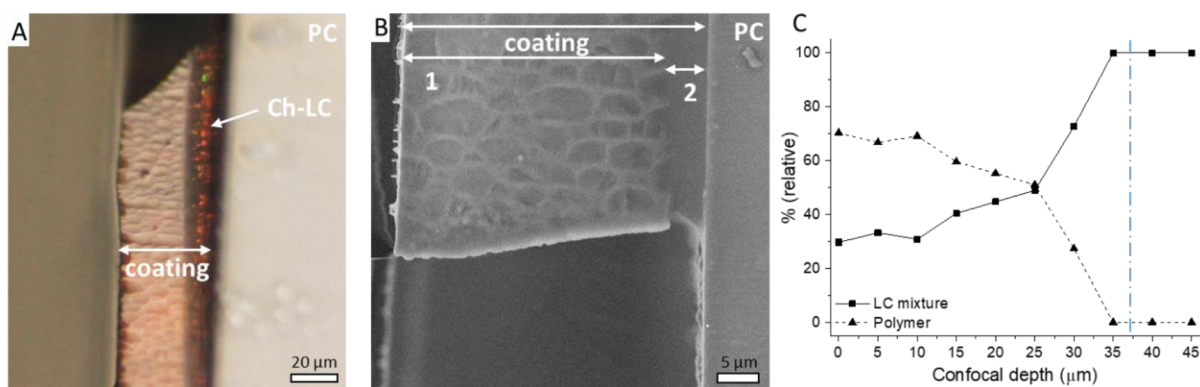
**Characterizations.** UV–vis spectroscopy was performed on a PerkinElmer LAMBDA 750 UV/vis/NIR spectrophotometer equipped with a 150 mm integrating sphere. Optical microscopy (OM) was done with a VHX-5000 KEYENCE digital microscope used in bright field. Scanning electron microscopy (SEM, JEOL JSM-7800F) was used to characterize some of the samples. The settings used were high vacuum, 10 kV acceleration voltage, 10 mm working distance, and backscatter electron detector. Cross sections of the samples (coating and substrate) were done by cryo-cutting. For SEM analysis, a 6 nm thick layer of Pd/Pt was sputtered at the surface of the samples. Raman spectroscopy measurements were performed on a Bruker SENTERRA dispersive Raman microscope. A confocal line scan was measured starting at the surface and measured every 5  $\mu\text{m}$  by using a 532 nm laser, 100 $\times$  objective, and 10 scans per step. The confocal resolution was  $\sim 20 \mu\text{m}$ .

## RESULTS AND DISCUSSION

**Body-Temperature-Responsive Reflector.** Photostratified Ch-LC coatings were fabricated by using a mixture (Figure 1) of acrylic monomers 1 (4 wt %) and 2 (46 wt %)



**Figure 2.** (A) Schematic representation of the fabrication method for the stratified coating via bar-coating and photopolymerization. The cured coating depicts the ideal case when polymerization occurs subsequently to the depletion induced diffusion. (B) Photographs of the polymerized coating at room temperature (namely 24  $^{\circ}\text{C}$ ) and skin temperature (namely 33  $^{\circ}\text{C}$ ). (C) Photograph of the coating heated by the skin, showing the flexibility of the coating and the substrate. (D) Transmission spectra of the polymerized coating at various temperatures, showing the cholesteric reflection bands of the coating between 22 and 45  $^{\circ}\text{C}$ . Below and above these temperatures, the coatings becomes smectic and isotropic, respectively. (E) Central wavelength of the reflection bands shown in (D) displayed at various temperatures showing the temperature-responsive curve of the coating.



**Figure 3.** (A) OM image of a cross sections of the stratified coating showing a narrow red-reflective layer in between the PC and a nonreflective top layer. (B) SEM image of a cross section of the coating, showing again a narrow layer in between the PC and the top layer. In this case, the LCs are no longer present due to the need for vacuum in the SEM chamber. In both images, part of the coating was lost during sample preparation. (C) Ratio between polymer formed and LC mixture using Raman spectroscopy. The blue dashed line indicates the thickness of the coating observed in (B).

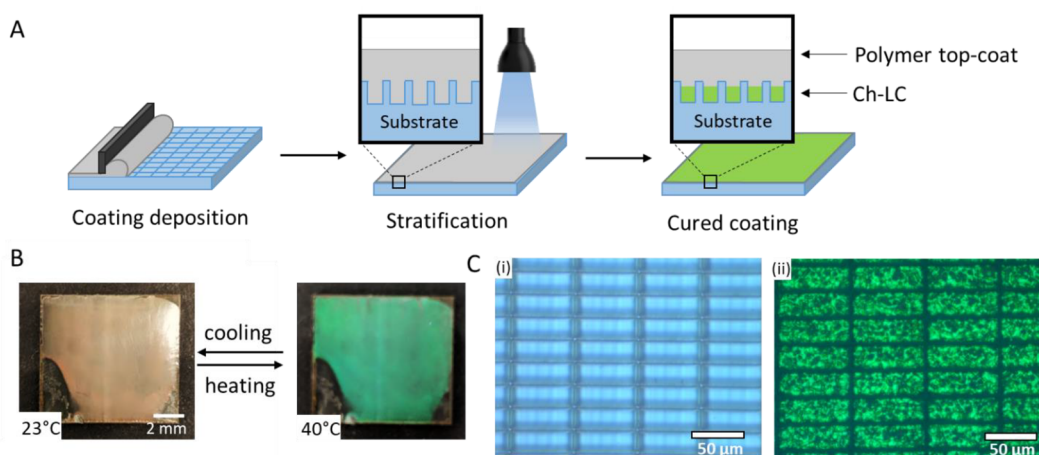
and a Ch-LC mixture (50 wt %). Acrylic monomers **1** and **2** were used to build up the hard top coat polymer layer.<sup>22</sup> Cross-linker **1** was added to enhance the rigidity of the polymer layer formed. Monoacrylate **2** was chosen because of its nonvolatile low-viscous nature. Furthermore, it remains transparent after polymerization while the glass transition temperature of poly-**2** of 110 °C is sufficiently high to create a hardened top coating. To increase the depletion-induced diffusion of the acrylic monomers to the top, UV-absorbing dye **4** was added in the mixture as well. For the formation of the mesogenic Ch-LC phase with a large temperature response near room temperature, i.e., between 17 and 49 °C, a ratio of 70 wt % MLC-2138 to 30 wt % chiral dopant was used. Below 17 °C, a smectic phase was obtained, and above 49 °C the mixture became isotropic. Because of the smectic to cholesteric LC phase transition temperature ( $T_{S-Ch}$ ) of the liquid crystals in the coating, cooling at a temperature just above the  $T_{S-Ch}$  causes unwinding of the helical alignment, which results in a strong pitch increase and red-shift of the reflection band. By adjusting the composition of the mesogenic mixture, the phase transition temperatures and the width of the Ch-LC temperature window could be tuned (Figure S2).

We first prepared photonic coating without trays to study the temperature-responsive optical properties. The combined mixture of acrylic monomers and nonpolymerizable LCs (Ch-LC Mixture) was coated on a flexible polycarbonate (PC) substrate. Polymerization of the acrylate monomers caused photoinduced phase separation of the polymer formed and the nonreactive mesogens. As a result, although the initial paint is fully transparent, removal of non-liquid-crystalline monomers allowed for the formation of a Ch-LC phase in between the polymer layer formed and the substrate, which is schematically shown in Figure 2A. Figure 2B shows photographs of the final coating, revealing the formation of a Ch-LC phase, as evidenced by the coating coloration. A reversible red to green color change can be achieved by solely using the difference between room temperature (namely 24 °C) and skin temperature (namely 33 °C) (Movie S1). Moreover, because of the maintained mobility of the LCs, shifting of the reflection band occurs in a matter of seconds.

Close to the  $T_{S-Ch}$ , cooling of a single degree causes the reflection band of the coating to red-shift for 100 nm, i.e., from 726 to 826 nm, caused by the rapid unwinding of the helix

(Figure 2C,D). A total reflection band blue-shift of 330 nm was observed when heating the coating from 22 to 45 °C.

To study the internal structure of the stratified temperature-responsive photonic coating, cross sections were analyzed by a variety of techniques. Note that due to nonpolymerized LC mesogens present in the coating, analysis of the cross sections of the coatings is challenging. Figure 3 shows both optical microscopy (OM) and scanning electron microscopy (SEM) images of cross sections of the coating. Remarkably, in the OM image (Figure 3A), a narrow color-reflective layer is present, indicating a photonic Ch-LC alignment sandwiched between the PC substrate and a thicker top layer. Analyzing a cross section of the coating using SEM (Figure 3B), we found similar layers, for which the top layer (1) has a thickness of  $\sim 32$  μm and the Ch-LC layer a thickness of  $\sim 5$  μm. The 37 μm thick coating has sufficiently phase-separated to lead to the creation of a continuous photonic Ch-LC inside the final coating, as is evidenced by the detection of a reflection band by UV-vis spectroscopy (Figure 2C). Nevertheless, it seems that the polymerization of the acrylic monomers took place before a perfect acrylic: LC bilayer structure could be formed. Because initially a ratio of 50/50 wt % acrylic monomers versus LC mesogens was used, theoretically a much thicker Ch-LC phase of  $\sim 18$  μm would be expected inside the phase-separated cell structure. Therefore, the top layer (1) most likely contains significant amounts of nonreactive LC mesogens as well, which does not contribute to the photonic reflection band. By use of confocal Raman spectroscopy, the ratio between the peak area at 2190–2250  $\text{cm}^{-1}$  corresponding to CN moieties in the mesogenic mixture and the peak area at 2800–3028  $\text{cm}^{-1}$  corresponding to the  $\text{CH}_2$  of monomer **2** was used to calculate the composition of the material through the thickness of the coating (Figure 3C). Because the  $\text{CH}_2$  of monomer **2** overlapped with the  $\text{CH}_2$  vibrational signals of the LC mixture and the PC substrate, calibration curves were made to separate the peak areas by using known ratios between the polymer formed and LCs and known ratios between the vibrational signals at 869–907 and 2800–3028  $\text{cm}^{-1}$  of the PC substrate. Although at a penetration depth between 0 μm (i.e., coating–air interface) and 25 μm, more polymer seemed to be present with respect to the LC mesogens, a significant number of mesogens were found at these penetration depths corresponding to layer 1 in Figure 3B. When measured further into the



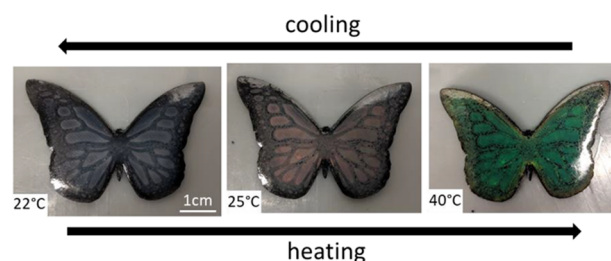
**Figure 4.** (A) Fabrication method of the coatings, using substrates with walls. (B) Photographs of the stratified coating at room temperature (i.e., 23 °C) and heated to 40 °C. (C) OM images of the structured substrates showing the laser etched rectangular boxes ( $60 \times 20 \times 20 \mu\text{m}^3$  in length, width, and height, respectively, with a wall thickness of  $2 \mu\text{m}$ ): (i) before the coating was applied and (ii) after the substrate was coated and polymerized, showing the reflective material inside the etched boxes.

coating, the polymer:LC ratio decreased. Above penetration depths of  $35 \mu\text{m}$ , only signals from the PC substrate and LCs were identified, indicating indeed a layer dominantly made of LC mesogens, as observed in Figure 3A,B. Note that the thickness of the coating is  $\sim 37\text{--}40 \mu\text{m}$ . However, during Raman analyses, LC signals were measured at penetration depths of  $45 \mu\text{m}$ , which is most likely caused by the confocal resolution of the equipment ( $\sim 20 \mu\text{m}$ ) or leakage of LCs during sample preparation of the cross sections of the coating.

**Temperature-Responsive Coatings on Substrates with Trays.** To see whether the CLC mixture can also be coated and stratified on a substrate with a tray, a PC substrate prepared with trays of  $24 \times 10^3 \mu\text{m}^3$  separated by  $2 \mu\text{m}$  thick walls was prepared by etching (Figure 4A). In this approach, walls are composed of polycarbonate, avoiding the need for masked-illumination steps. To create wall structures, a PC substrate was used in which rectangular boxes of  $60 \times 20 \times 20 \mu\text{m}^3$  (length  $\times$  width  $\times$  height) were etched. Note that the height of the walls is smaller than the  $40 \mu\text{m}$  thickness of the coating. However, since the thickness of the photonic layer is  $\sim 5 \mu\text{m}$  (*vide infra*), the acrylic polymer layer should be anchored to the wall architecture after stratification. Again, the Ch-LC mixture was applied to the substrate and polymerized similarly to the ones discussed in Figure 2. Photographs of the coating (Figure 4B) reveal that trays are not visible with the naked eye. The resulting coating shows a good alignment as illustrated by the red reflective color. Temperature-responsive behavior is similar to the coating without trays (Figure 2). Upon heating the coating reversibly blue-shifts from red to green within seconds, after which it becomes isotropic at temperatures higher than  $50 \text{ }^\circ\text{C}$ . Figure 4C shows an optical microscope image of the substrate before and after stratification. The photonic reflection of the Ch-LC mesogens in the coating was only present inside the rectangular boxes of the substrate (Figure 4C(ii)), which indicated that the walls are most likely connected to the acrylic polymer top layer. Macroscopically, the adhesion of the coatings was significantly enhanced. While coatings without these wall structures are easily movable across the substrate by rubbing, these coatings are far more resistant toward such displacement.

As a next step 3D printing was used to create tray structures of any desired shape that can be filled with the Ch-LC mixture.

In this case, a butterfly was 3D printed from black PLA polymer filament. All layers except the final one were completely filled by the PLA polymer, serving as the 2 mm thick substrate. The final  $\sim 200 \mu\text{m}$  thick layer contained trays in the wing while printing only the veins and contour of the butterfly, serving as the walls (Figure S1). Subsequently, the ink (Ch-LC mixture) was applied by using bar-coating and was exposed to light to induce the stratification. Figure 5 shows the



**Figure 5.** 3D-printed butterfly (polymer: poly(lactic acid) (PLA)). The veins have an additional printed layer with respect to the rest of the butterfly. Heating the coating causes a photonic color change of the Ch-LC mesogens

printed butterfly coated with the temperature-responsive paint at various temperatures. As the layer thickness of the walls had increased and the coating covered the entire substrate (i.e., including the veins and edge), the final coating had an increase in thickness of  $\sim 200 \mu\text{m}$ . Nevertheless, after the fabrication process, again a well-aligned encapsulated Ch-LC layer was obtained on the PLA substrate, as was evidenced by the structural coloration of the butterfly. The coating was heated and cooled, showing again a similar reversible temperature-responsive behavior similar as shown before (Figures 2 and 4), having a reversible blue-shift of the reflection band upon heating between 22 and  $\sim 50 \text{ }^\circ\text{C}$ , shifting the color from the IR light at  $22 \text{ }^\circ\text{C}$  to green at  $40 \text{ }^\circ\text{C}$  within seconds. Also in this case, the coating can be rubbed without movement of the coating across the substrate, indicating the open spaces in the wings to be filled partially with the photonic Ch-LC mesogens, anchoring the acrylic polymer top layer to the veins and edge.

## CONCLUSION

Photoinduced phase separation was used to create temperature-responsive encapsulated Ch-LC coatings on flexible substrates. Using a mesogenic component having a smectic to cholesteric phase transition temperature, coatings were fabricated, needing only a few seconds and 1 °C temperature difference to shift the IR reflection band of 100 nm and a total reflection band shift of 330 nm while heating from 22 to 45 °C.

Subsequently the linkage between the substrate and the polymer top layer was studied by creating walls from the substrate increasing the coating adhesion. Moreover, a butterfly with walls was 3D-printed and coated with the temperature-responsive paint, showing the ability to coat arbitrary-shaped substrates with the temperature-responsive paint. The CLC mixture can be easily aligned in the trays, giving clear visible structural colors. These coatings displayed enhanced adhesion and a similar temperature-responsive behavior as the coatings prepared without walls. Various other processes relying on stamping or selective material addition or removal can be thought of as well to produce defined structured substrate surfaces. Such photonic reflectors with arbitrary shapes are potentially interesting for sensors, surfaces with tunable aesthetics, or anticounterfeit labels, which might require sensitivity to small temperature variations close to room or body temperature and reaction times within seconds.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsapm.9b00841.

Schematic drawing of the 3D-printed butterfly, DSC diagrams of the mesogenic mixture varying the chiral dopant concentration, fabrication, and analyses of masked-illuminated coatings (PDF)

Movie showing the reflection band shift when heating from room temperature to body temperature (MP4)

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### Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

PC, polycarbonate; PLA, poly(lactic acid); Ch-LC, cholesteric liquid crystal; OM, optical microscopy; SEM, scanning

electron microscopy;  $T_{S-Cb}$ , smectic to cholesteric liquid crystalline phase transition temperature; IR, infrared.

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