# **Supporting Information**

# An easily coatable temperature responsive cholesteric liquid crystal oligomers for making structural colour patterns

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# **Experimental section**

# Materials

The diacrylate (compound 1) and chiral dopant (compound 2) were purchased from Jiangsu Hecheng Advanced Materials Co. Ltd. n-butylamine was obtained from Shanghai Macklin Biochemical Co., Ltd. Tetrahydrofuran (THF) and dichloromethane (DCM) were purchased from Tianjin Zhiyuan Chemical Co., Ltd. Photoinitiator Irgacure 184 was obtained from Tianjin Heowns Biochem Technologies LLC. 2-(N-ethylperfluorooctanesulfonamido) ethyl methacrylate was used as surfactant and was purchased from Shen Zhen Reagent Biotechnology Co.,Ltd. Poly(vinyl alcohol) (PVA) was purchased from Sigma-Aldrich, Inc.

# Methods

*Nuclear Magnetic Resonance (NMR).* The oligomer was characterized by <sup>1</sup>H-NMR (Varian AS400; 400 MHz), using chloroform-d as solvent.

Differential scanning calorimetry (DSC). DSC curves were measured with a Mettler Toledo DSC

1 from Mettler Toledo, using a rate of 5 °C/min for both heating and cooling cycles.

*Polarized optical microscopy (POM).* POM images were taken using a Leica CTR6000 polarized optical microscope, equipped with a Leica DFC 420C camera. Temperature was controlled using a Linkam temperature control stage (Linkam PE95/T95).

*Transmission spectra.* Transmission spectra were obtained with a UV/VIS/NIR spectrometer (Perkin Elmer Lambda 950). Temperature of the sample was controlled by a water-agent temperature controller (EYELA NCB-1200).

*Thickness and surface topography measurements.* The thickness of the coatings and the surface topographies were measured with a 3D profilemeter (Leica DCM8).

*WAXS.* The coatings for SAXS measurement were prepared by curing at different temperatures. And the coatings were then analyzed by WAXS (Ganesha lab instrument).

*Preparation of the oligomer.* The oligomers used for coating were prepared as follows: 1788.6 mg RM82, 199.9 mg n-butylamine and 235.3 mg LC756 were added in a 20ml glass vial and dissolved in 5ml DCM. The mixture was stirred at 20 °C for 24 hours, after which the DCM was removed at 100 °C for 1 hour and THF was added instead. The mixture was stirring at 100 °C for another 18 hours. And the THF was allowed to evaporate during the oligomerization. In the end, the THF was

further removed in a vacuum oven at 50 °C overnight.

*Polyvinyl alcohol functionalized glass.* To prepare a polyvinyl alcohol functionalized glass substrate,  $3 \times 3 \text{ cm}^2$  glass plates were cleaned in acetone for 30 minutes using ultra-sonication, followed by 30 minutes in ethanol and subsequently UV-Ozone treatment (PR-100, Ultra Violet Products) for 20 minutes. 5 wt% polyvinyl alcohol with a molecular weight of 6000 was dissolved in distilled water and spin-coated on a clean  $3 \times 3 \text{ cm}^2$  glass plate using a spin coater (Karl Suss CT 62) by rotating at 2500 rpm for 30 s. The polyvinyl alcohol coated glass plates were then placed at 60 °C for 30 minutes and were then rubbed on a velvet cloth.

*Preparation of the coating.* To prepare the coating mixture, 167.7 mg (78 wt%) of the oligomer was mixed with 2.2 mg (1 wt%) photoinitiator, 2.2 mg (1 wt%) surfactant, and 42.2 mg (20 wt%) THF. For the control experiment, 253.9 mg (94.5 wt%) of the compound 1 was mixed with 9.3 mg (3.5 wt%) compound 2, 2.7mg (1 wt%) Irgacure184 and 2.7 mg (1wt%) surfactant. The mixture was then applied on a glass substrate using a thin film applicator (BEVS) at a desired temperature with a 10µm gap of a 4-sided applicator (10 to 20µm gaps, BEVS) which was automatically pushed forward over the mixture with a speed of 15 mm/s. The coatings with THF in then stayed at 55 °C for 30 min to remove THF before photopolymerization or band shift measurement.

*Photopolymerization.* Photopolymerization of the coatings was done in a nitrogen box using an EXFO Omnicure S2000 mercury lamp in the range 320-390 nm at a desired temperature.

*Preparation of coatings with patterns.* To prepare the coating with different patterns, 2 wt% LC756 was added to the oligomer to prepare coatings that reflect visible light. Masks with different openings made of black paper were used. After preparation of the coating, it was exposed through a mask and cured locally at desired temperature for 15 s with a UV light intensity of 0.3 mW/cm<sup>2</sup> followed by a flood curing at 20 °C for 10 min with a UV light intensity of 2 mW/cm<sup>2</sup>. By being exposed to UV light at different temperatures, coatings with coloured patterns were prepared.

# 1. Synthesis and Crosslinking of Cholesteric Liquid Crystal Oligomers



**Figure S1.** Two-step synthetic route to fabricate crosslinked cholesteric liquid crystal networks.<sup>S1</sup>

2. DSC



Figure S2. DSC curve of cooling and heating for the main-chain LC oligomer.

# 3. NMR



**Figure S3.** <sup>1</sup>H NMR spectrum of the oligomer. The average degree of polymerization was calculated by the ratio between acrylate end group **a**, **b**, **c** with a value of 0.76 respectively and aromatic methyl group **f** with a value of 3 as follows, DP=2/0.76=2.6.



# 4. Temperature Response Before Oligomerization Reflection band of the Monomers

**Figure S4.** Spectra of the uncured coating based on the monomer 1 and 2 mixture measured at various temperatures. A) Measured by heating from 86 °C to 108°C. B) Measured by cooling from 86 °C to 32°C.



#### 5. Temperature Response After Oligomerization

**Figure S5.** Transmittance spectrum at various temperatures of the oligomer coating shown in Figure 2A measured after 1.5 months.

# 6. Cured coating



**Figure S6.** Optical properties of cured oligomer coating. A) Photographs of the coating at viewing angle of 45 °. B) Polarized optical microscopy images of the polymer coating under crossed polarizer at room temperature. C) Fully crosslinked coating by curing at 50 °C for 10 min. D) Angle dependent transmission spectra of the coating at room temperature.

# 7. Patterned coatings



Figure S7. Reflection band of a coating before crosslinking, with a reflection band in

the visible range, measured at temperature ranging from 23°C to 55°C.



Figure S8. Photographs of the crosslinked coatings with different two colour patterns.



**Figure S9.** Polarized optical microscopy images (in incidence light mode) of (A) letter "I", (B) letter "M" and (C) letter "R", indicating good resolution of the pattern.



**Figure S10. Stability of the coatings.** (A) Transmittance spectra of the coating with a "Star" pattern measured before and after treatment at 80 °C on a hot plate for 24 hours and 48 hours. (B) Transmittance spectra of a coating measured before and after exposure to a sun tester for 20 hours at 30 °C, 0.55 W/m<sup>2</sup> at 340nm.

#### References

S1. T. H. Ware, M. E. McConney, J. J. Wie, V. P. Tondiglia and T. J. White, *Science*, 2015, **347**, 982–984.