Supporting Information

for *Adv. Mater.*, DOI: 10.1002/adma.202103309

Anisotropic Iridescence and Polarization Patterns in a Direct Ink Written Chiral Photonic Polymer

*Jeroen A. H. P. Sol, Henk Sentjens, Lanti Yang, Nadia Grossiord, Albertus P. H. J. Schenning,* and *Michael G. Debije*
Supporting Information

Anisotropic iridescence and polarization patterns in a direct ink written chiral photonic polymer

Jeroen A. H. P. Sol, Henk Sentjens, Lanti Yang, Nadia Grossiord, Albertus P.H.J. Schenning*, Michael G. Debije*

Video Files

**Video S1.** Coating on PET foil, made with ChLC oligomer ink catalyzed by 5. Video recorded with the sample rotating at 4° s⁻¹; video playback rate set to 500 %.

**Video S2.** Coating on glass, made with ChLC oligomer ink catalyzed by 5, with the “Sfd” area polymerized at 40 °C, the remainder at 70 °C. Video recorded with the sample rotating at 4° s⁻¹; video playback rate set to 500 %.

**Video S3.** The print process as it happens, showing the phase transitions the chiral nematic ink is undergoing immediately after deposition on the glass substrate at 53 °C.

**Video S4.** The *Morpho*-inspired print from Figure 5d in the main text shown on a rotating table. Video recorded with the sample rotating at 4° s⁻¹; video playback rate set to 500 %.

**Video S5.** The arrow-shaped signaling device from Figure 5f in the main text shown on a rotating table. Video recorded with the sample rotating at 4° s⁻¹; video playback rate set to 500 %.
**Video S6.** The print process for the unidirectionally aligned arrow, showing repeated airborne movements necessary for the desired alignment direction.

In Videos S1, S2, S4, and S5, the camera was positioned at circa 50° from the surface normal direction of the substrates, and the light source (a halogen bulb guided through an optical fiber) was set to illuminate the sample from the same location as the camera (see Figure S19).
Methods:

Formulation considerations

In other research works detailing (chiral nematic) liquid crystal elastomers,[1–5] different reactive mesogens are often used to build up these networks, such as “RM82” (CAS No. 125248-72-8) and “RM257” (CAS No. 174063-87-7) from Merck KGaA. Here, we have chosen for BASF’s “LC 242” (1) since this molecule is known to form stable chiral nematic phases when not chain extended.29 Chiral dopant 2 (BASF’s “LC 756”) is a staple chiral diacrylate in the field of liquid crystal engineering for its high helical twisting power, meaning that only a small weight fraction of the dopant is needed to achieve light reflection in the visible spectrum range.[6] Dithiol 3 is used since it has been used successfully in past research, but unlike low molecular weight alkylene dithiols, it is not as pungent, and thus more comfortable to work with.[7]

Oligomer chain length determination

From the spectra shown in Figure S1, one can calculate an average chain length through comparing the signal integrals for the acrylate protons (δ 5.8-6.5 ppm) versus protons on the phenyl ring in the liquid crystal core (δ 8.2-8.3 ppm). Setting the integral for the acrylate protons to 6 effectively normalizes the spectrum to a single chain—as we use an excess of acrylate for the reaction, we assume that each ChLC oligomer molecule is capped on both α and ω positions by an acrylate group (hence, 2 sets of 3 acrylate protons). The signal at (δ 8.2-8.3 ppm) covers 4 protons, so dividing this integral by 4 then gives the number of mesogenic cores present on average in the oligomer:[8]

\[ x_a = \frac{I(8.2-8.3 \text{ ppm})}{4} \]
It is important to note $x_n$ describes the number of LC molecules in an average oligomer; the actual degree of polymerization (DP) as used in Carother’s equation requires consideration of the incorporated dithiol chain extenders as well. To convert $x_n$ to DP, the following equation is used:

$$DP = 1 + 2(x_n - 1)$$

Using DP one can then calculate the reaction conversion based on the initial excess of diacrylate over dithiol, for instance.

From $x_n$ the average oligomer molecular weight is determined using:

$$M_n = \left( \frac{n_1}{n_1 + n_2} M_1 + \frac{n_2}{n_1 + n_2} M_2 \right) + (x_n - 1) \left( \frac{n_1}{n_1 + n_2} M_1 + \frac{n_2}{n_1 + n_2} M_2 + M_3 \right)$$

where $n_i$ is the amount of mols of LC 1 or 2 used for the reaction, and $M_j$ is the molecular weight of component 1, 2 or 3, as indicated by the subscript value.

With the equations given here, we calculate the following data for the materials used in this report:

Additional data on the oligomers formed was obtained from GPC, while not showing the exact molecular weights contained in the mixes of oligomers synthesized, does allow for calculation of the dispersity index $D = M_w / M_n$. The integration boundaries for this calculation have been set to include any signal that comes in from the onset of measuring up to about 17 min, which corresponds to the elution time of reactive liquid crystal 1.
From the data in Figure S2, corresponding to the oligomer made for direct ink writing, we find $D = 2.033$.

**Thiol-acrylate Michael addition considerations**

Comparing the $^1$H-NMR spectrum of this ink with that of a thiol-acrylate LCE ink based on different reactive mesogens,\[^8\] there are a few signals that stand out in Figure S1. The signal at $\delta$ 3.1 ppm is indicative of the compound with $m/z = 352.46$ in Figure S3, and $\delta$ 6.9 ppm, $\delta$ 8.1 ppm indicate phenolic groups formed as by-products from the exchange reaction between the carbonate groups on 1 and 2 and the thiol group on 3. In this case the thiol proton is transferred to the phenyl-bound oxygen, and the sulfur on the thiol forms a thiocarbonate with the C$_4$ spacer group.

Additionally, MALDI-ToF-MS results also point to the formation of by-products from this reaction. Specifically, the exchange reactions also show up during mass spectrometry. In Figure S4 the product of the side reaction on monomer 1 is shown, but this likewise happens with chiral monomer 2.

These by-products are found in the mass spectrum at $\Delta(m/z) = -170.53$, and are found around the expected peaks for the monomers of both 1 and 2, as well as dimers, trimers, and tetramers. The third compound, with $m/z = 352.46$ also a by-product of the side reaction, is not found in the spectrum itself, but different signals with this offset are found, hinting at the possibility that this compound has been incorporated into oligomers during the reaction procedure. Unfortunately, since the peak intensities found in MALDI-ToF-MS are highly dependent on the experimental conditions during the analysis, we cannot use these for quantitative analysis.\[^9\] As such, for the rate at which these by-products are formed, we are
mostly reliant on $^1$H-NMR, as detailed earlier. We have not identified any ill effects resulting from these side reactions from either our coating or direct writing results.

From MALDI-ToF-MS analysis, a number of expected compounds can be identified. These are monomers of:

1 (calcd. $m/z$ 705.2 [M + H$^+$], observed 705; calcd. $m/z$ 727.2 [M + Na$^+$], observed 726; calcd. $m/z$ 743.3 [M + K$^+$], observed 743),

3 (calcd. $m/z$ 205.0 [M + Na$^+$], observed 205; calcd. $m/z$ 221.1 [M + K$^+$], observed 219);

2 is not observed due to the low molar fraction of it in the material (2.45 mol %).

Dimers:

1-3-1 (calcd. $m/z$ 1613.4 [M + Na$^+$], observed 1612; calcd. $m/z$ 1629.6 [M + K$^+$], observed 1630),

Trimers:

1-3-1-3-1 (calcd. $m/z$ 2500.7 [M + Na$^+$], observed 2501; calcd. $m/z$ 2516.8 [M + K$^+$], observed 2516),

1-3-1-3-2 (calcd. $m/z$ 2762.8 [M + Na$^+$], observed 2763),

Tetramers:

1-3-1-3-1-3-1 (calcd. $m/z$ 3404.0 [M + Na$^+$], observed 3403),

1-3-1-3-1-3-2 (calcd. $m/z$ 3649.0 [M + Na$^+$], observed 3649)

Pentamers:

1-3-1-3-1-3-1-3-1 (calcd. $m/z$ 4103.3 [M + H$^+$], observed 4103),
Optical characterization of the crosslinked materials

**Angle-dependent UV-vis transmission characterization**

Angle-dependent UV-vis spectra were recorded using the PerkinElmer Lambda 750 spectrophotometer with an OMT Solutions ARTA goniometer sample stage detector. The sample stage angle is controlled by software and sets the sample angle to the desired value before measuring. Since this detector module is limited to linear polarized light, only data for 0° polarization (parallel to rotation axis of sample) is reported.

**Angle-dependent optical characterization**

Sample photography for different sample orientations was done by placing the sample on a rotating stage, which allowed to set different azimuthal angles $\phi$. Polar angle $\theta$ was set by changing the height of the camera on the tripod.

**Angle-dependent UV-vis reflection characterization**

For studies on angle-dependent light reflection, a Melchers Autronic DMS 703 LCD characterization device was used. This device allows for optical characterization of transmissive materials while modifying the sample angle ($\theta$) and the angle at which the detector arm is raised from the surface normal ($\phi$).

The machine illuminates the sample from below using a halogen light source, and an optical fiber attached to the moving arm captures the transmitted light. This is recorded for a blank glass slide (borosilicate) and a glass slide coated with the slanted chiral nematic LCE, or a planar reference chiral nematic LCN. The chiral nematic spectra are subtracted from the glass
transmission spectrum to generate curves where the peak value is the main reflected
wavelength, a function of both $\theta$ and $\phi$. This corresponds to the data presented in Figure 2b.
Since the slanted chiral nematic is symmetric over the “bar coating axis” and the reference
chiral nematic is axially symmetric around the surface normal, only azimuthal angles $0 < \phi < 180^\circ$ have been measured.

**Polarization-dependent optical characterization**

Photographs were recorded using an optical camera with a circular polarization filter held
between the camera and sample. To compensate for the darkened image caused by the
polarization filter, images were compensated by +1.20 EV in Adobe Lightroom.

**Polarization-dependent UV-vis transmission characterization**

Circular polarization dependent UV-vis transmission measurements were performed on a
Shimadzu UV-3102 PC spectrophotometer with a linear polarizer-$\lambda/4$ stack. The linear
polarizer-$\lambda/4$ stack gives true circularly polarized light at 633 nm.
For measurements, a baseline was recorded on cleaned glass slides without coating, after
which the slanted chiral nematics were measured for both left and right circular polarized
light across the visible spectrum.

**Polarization-dependent UV-vis reflectance characterization**

Circular polarization dependent UV-vis reflectance measurements were performed on a
PerkinElmer Lambda 750 spectrophotometer with a linear polarizer-$\lambda/4$ stack and integrating
sphere detector.
Measurements were done with the baseline measured in without sample nor substrate, through
the linear polarizer and $\lambda/4$-plate (usable for $\lambda > 380$ nm). Using a reference right-handed
chiral nematic film, the linear polarizer was rotated stepwise to find the positions of pure left
and right circular polarized light, from reflection minima and maxima, respectively. Knowing these positions, the setup was used to measure UV-vis reflectance spectra for left and right circular polarized light.

**Polarization-dependent, angle-dependent optical characterization**

The simultaneous measurement of polarization-dependence and angle-dependence was not possible with the equipment available in the lab, and is thus instead done using circular polarization filters and an optical camera; here the sample was placed in a photo studio box on a rotating table (to allow for adjusting $\phi$), while the position of the camera with respect to the sample table allowed for adjustment of $\theta$. A circular polarization filter was placed between the camera and sample.

Since photographs taken at equal exposure appear darker through the circular polarization filter, the exposure value of these photos was increased by +1.20 EV in Adobe Lightroom.
Table S1. Compounds used for synthesis of the chiral nematic liquid crystal oligomer ink.

|   | Description                                                                 | Molecular Formula | Molecular Weight (g mol⁻¹) | CAS No.    |
|---|------------------------------------------------------------------------------|-------------------|----------------------------|------------|
| 1 | BASF Paliocolor® LC 242 (reactive nematic liquid crystal)                     | C₁₇H₉₀O₁₄         | 704.68                     | 187585-64-4|
| 2 | BASF Paliocolor® LC 756 (reactive chiral dopant)                             | C₅₀H₄₆O₂₀         | 966.9                      | 223572-88-1|
| 3 | 2,2′-(ethylenedioxy)diethanethiol (dithiol chain extension agent)           | C₆H₁₄O₂S₂         | 182.3                      | 14970-87-7 |
| 4 | 1,8-diazabicyclo[5.4.0]undec-7-ene (base thiol-acrylate catalyst)            | C₉H₁₆N₂           | 152.24                     | 6674-22-2  |
| 5 | dimethylphenylphosphine (nucleophilic thiol-acrylate catalyst)                | C₈H₁₁P            | 138.15                     | 672-66-2  |
| P1| Ciba Irgacure® 819 (photo-activated free radical polymerization initiator)    | C₂₆H₂₇O₃P         | 418.47                     | 162881-26-7|
| 7 | Ciba Irgacure® 184 (photo-activated free radical polymerization initiator)    | C₁₃H₁₈O₂         | 204.26                     | 947-19-3  |
Table S2. Calculated $x_n$, DP, and $M_n$ values from $^1$H-NMR data.

| ChLC oligomer ink synthesized with… | $x_n$ (-) | DP (-) | $M_n$ (g mol$^{-1}$) |
|----------------------------------|-----------|--------|----------------------|
| …catalyst 4                      | 2.59      | 4.18   | 2143.6               |
| …catalyst 5                      | 2.31      | 3.62   | 1892.6               |

Table S3. Phase transitions measured using DSC during cooling. 5 K min$^{-1}$ (* 10 K min$^{-1}$).

| ChLC oligomer ink synthesized with… | $T_g$ (°C) | $T_{NI}$ (°C) |
|----------------------------------|------------|---------------|
| …catalyst 4                      | -30        | 70            |
| …catalyst 5 *                    | -22        | 76            |
**Figure S1.** 400 MHz proton nuclear magnetic resonance (¹H-NMR) spectra of the ChLC oligomer ink materials made with catalyst 4 for bar coating (top) and direct ink writing (middle) and catalyst 5 (bottom). Material dissolved in chloroform-d, spiked with 0.03 % v/v tetramethylsilane for reference (δ 0 ppm).
Figure S2. Gel permeation chromatogram of the chiral nematic liquid crystal oligomer ink made for direct ink writing using catalyst 5 dissolved 1 mg mL$^{-1}$ in tetrahydrofuran. The calibrant for this GPC device is polystyrene (PS).
**Figure S3.** Side products that are suspected of being formed when the thiol group reacts with the carbonate group present in the reactive mesogens.
Figure S4. MALDI-ToF-MS spectrogram for the ink material made for DIW using catalyst 5, as found for both MALDI matrices CHCA and DCTB.
Figure S5. Differential scanning calorimetry (DSC) trace of the chiral nematic liquid crystal oligomer ink (catalyst 5), measured at 10 °C min⁻¹. Plotted as “Exo up”, the cooling cycle is the upper half of the plot, while the heating cycle is the lower half.
**Figure S6.** The chiral nematic liquid crystal oligomer ink (catalyst 5) viewed using a polarized optical microscope, with the sample between crossed polarizers.
Figure S7. Slanted chiral nematic coating seen from different angles exposed to unpolarized light from directly overhead. The ink used here was made using catalyst 4.
Figure S8. Dynamic mechanical thermal analysis (DMTA) of a crosslinked, printed ChLCE film (material: catalyst 5). In this case, the sample as heated to 100 °C, cooled to -90 °C and reheated to 100 °C; the second heating run is shown here (5 °C min⁻¹).
Figure S9. Polarization-specific UV-vis spectrophotometric measurements showing the transmission characteristics for the material made with catalyst 4, coated on 75 µm thick PET foil. Baseline set to air.
Figure S10. (a) Data generated by the three-dimensional optical characterization device after processing, in this case for a slanted chiral nematic coating, where increasing polar angle \( \theta \) shows a red shifted reflection peak. (b) Scheme of the device used for this characterization, and definition of the two angles, polar (\( \theta \)) and azimuthal (\( \phi \)).
Figure S11. Same data as Figure 2c: two-dimensional optical characterization of a normal, planar cholesteric LC network coating (left) and of a bar coated ChLCE (right), plotted using a perceptually uniform color map (“viridis”).
Figure S12. Additional AFM images for bar coated ChLCE on PET foil. The scale bar represents 2 µm and corresponds to all five stitched images. (Left) AFM phase images, (right) fast Fourier transforms (FFT) obtained from the stitched images using ImageJ/Fiji. ¹⁰

The following data was extracted from this figure:

| Coatings made with catalyst 5                        | Coatings made with catalyst 4                        |
|-----------------------------------------------------|-----------------------------------------------------|
| (1) 30° ±0.18 µm half-pitch                         | (3) 40° ±0.18 µm half-pitch                         |
| (2) 28° ±0.18 µm half-pitch                         | (4) 41° ±0.22 µm half-pitch                         |
| (5) Figure 2d in the main text                      |                                                     |
|                                                     | 45° ±0.18 µm half-pitch                             |
|                                                     | (6) 48° ±0.18 µm half-pitch                         |
**Figure S13.** UV-vis reflectance spectra for the four printed samples shown in Figure 4b.
| Thickness set: 75 µm | Thickness set: 100 µm |
|---------------------|---------------------|
| 2 mm s⁻¹ |
| Actual sample thickness: | 62.3 ± 4.9 µm |
| | 54.7 ± 3.8 µm |
| 4 mm s⁻¹ |
| Actual sample thickness: | 64.9 ± 3.8 µm |
| | 31.5 ± 4.0 µm |
| 6²/₃ mm s⁻¹ |
| Actual sample thickness: | 44.4 ± 3.1 µm |
| | 32.4 ± 3.1 µm |
Figure S14. Angle-dependent UV-vis transmission spectra for printed ChLCE strips at different lateral nozzle speeds. The legend in the top right indicates the polar angle $\theta$, azimuthal angle $\phi = 0^\circ$ is kept constant.
| Thickness set: 75 µm | Thickness set: 100 µm |
|---------------------|----------------------|
| 2 mm·s⁻¹             |                      |
| Actual sample thickness: 62.3 ± 4.9 µm | Actual sample thickness: 54.7 ± 3.8 µm |
| 4 mm·s⁻¹             |                      |
| Actual sample thickness: 64.9 ± 3.8 µm | Actual sample thickness: 31.5 ± 4.0 µm |
| 6.25 mm·s⁻¹          |                      |
| Actual sample thickness: 44.4 ± 3.1 µm | Actual sample thickness: 32.4 ± 3.1 µm |
**Figure S15.** Peak positions extracted from angle-dependent UV-vis transmission spectra for printed ChLCE strips at different lateral nozzle speeds (see Figure S14). The angle noted on the x-axis relates to polar angle $\theta$, azimuthal angle $\phi = 0^\circ$ is kept constant. Blue squares (■) and squares (■) represent reflection peaks, the red squares generally of lower intensity. Black squares (■) are points estimated from weaker signals, such as shoulders.
**Figure S16.** Printed lines at different lateral nozzle speeds, from 1 to 15 mm s\(^{-1}\). The illumination direction is the same as the observation direction.
Figure S17. Schematic drawing: our proposed mechanism for transition from a planar cholesteric at low $v_{\text{nozzle}}$ to slanted cholesteric at high $v_{\text{nozzle}}$, and the intermediate state as reconstructed from UV-vis data (Figure S14, S15, S17). Plot: circular polarization-dependent UV-vis reflectance spectra recorded from samples printed at different $v_{\text{nozzle}}$ values.
Figure S18. Polarization-dependent reflection found for a butterfly pattern printed at two different printing speeds, 2 mm s\(^{-1}\) (outer) and 10 mm s\(^{-1}\) (inner). This shows that exclusively with print speed, different polarization selective reflectivity can be encoded in the material; the butterfly that inspired this print uses a similar property for communication.
Figure S19. Photograph detailing the setup used for recording of Videos S1, S2, S4, and S5. (unrelated sample displayed on table in this photograph)
Figure S20. Reflectance measurements at fixed wavelength $\lambda$. The linear polarizer is rotated, while the $\lambda/4$-plate is kept fixed, which results in different circular and elliptical polarization states. Using a reference right-handed chiral nematic film, pure LCP and RCP are determined.
**Figure S21.** Visible spectrum reflectance measurements for both LCP and RCP light.
Figure S22. Slanted chiral nematic coating on PET substrate observed from the front (noted ‘FRONT TILT’, observation polar angle $\theta \approx 50^\circ$), comparing the circular polarization of reflected light. ‘TOP VIEW’ shows the coating as seen from directly overhead, and its circular polarization characteristics.
Figure S23. Photographs of direct ink written ChLCE where the print path had a back-and-forth (left) or unidirectional (right) character. Different images correspond to different polarizations of reflected light: unpolarized (top), left circular polarized (middle), right circular polarized (bottom). Samples observed at circa 50° from the substrate normal direction.
Figure S24. Photographs of direct ink written ChLCE where the print path had a back-and-forth (left) or unidirectional (right) character. Different images correspond to different polarizations of reflected light: unpolarized (top), left circular polarized (middle), right circular polarized (bottom). Samples observed from the substrate normal direction.
**Figure S25.** Transmission polarized optical microscopy of 75 µm thick strips printed using three different methods: at 2 mm s\(^{-1}\), 10 mm s\(^{-1}\), and 10 mm s\(^{-1}\) in a single direction. “0-90” and “45-135” denote the positions of the polarizer and analyzer, respectively, while LCP and RCP indicate the light coming from the microscope light source as being left- (LCP) or right-handed circularly polarized (RCP). The photographed area represents ca. 2600 × 2000 µm\(^2\) for all images.
Supporting references

[1] A. Kotikian, R. L. Truby, J. W. Boley, T. J. White, J. A. Lewis, *Adv. Mater.* **2018**, *30*, 1706164.

[2] P. Zhang, G. Zhou, L. T. de Haan, A. P. H. J. Schenning, *Adv. Funct. Mater.* **2021**, *31*, 2007887.

[3] E. P. A. van Heeswijk, L. Yang, N. Grossiord, A. P. H. J. Schenning, *Adv. Funct. Mater.* **2020**, *30*, 1906833.

[4] M. López-Valdeolivas, D. Liu, D. J. Broer, C. Sánchez-Somolinos, *Macromol. Rapid Commun.* **2018**, *39*, 1700710.

[5] C. P. Ambulo, J. J. Burroughs, J. M. Boothby, H. Kim, M. R. Shankar, T. H. Ware, *ACS Appl. Mater. Interfaces* **2017**, *9*, 37332.

[6] C. Mock-Knoblauch, O. S. Enger, U. D. Schalkowsky, *SID Symp. Dig. Tech. Pap.* **2006**, *37*, 1673.

[7] A. H. Gelebart, M. K. McBride, A. P. H. J. Schenning, C. N. Bowman, D. J. Broer, *Adv. Funct. Mater.* **2016**, *26*, 5322.

[8] D. J. Roach, X. Kuang, C. Yuan, K. Chen, H. J. Qi, *Smart Mater. Struct.* **2018**, *27*, 125011.

[9] W. Yan, J. A. Gardella, T. D. Wood, *J. Am. Soc. Mass Spectrom.* **2002**, *13*, 914.

[10] J. Schindelin, I. Arganda-Carreras, E. Frise, V. Kaynig, M. Longair, T. Pietzsch, S. Preibisch, C. Rueden, S. Saalfeld, B. Schmid, J.-Y. Tinevez, D. J. White, V. Hartenstein, K. Eliceiri, P. Tomancak, A. Cardona, *Nat. Methods* **2012**, *9*, 676.