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Supporting Information

Spatial and Temporal Patterning of Polymers in Electric Field Responsive LC Templates

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Synthesis of AzoPIC

Instrumentation. All chemicals were used as obtained, unless otherwise stated. Silica gel (0.040-0.060 mm) from Merck was used for column chromatography and silica gel 60 F_{254} coated glass plates (Merck) were used for thin layer chromatography. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Inova 400 MHz or a Bruker Avance III 500 MHz spectrometer at room temperature. Chemical shifts are reported in ppm relative to tetramethylsilane (δ = 0.00 ppm). The following measurements were recorded at room temperature unless stated otherwise. UV-VIS spectra was performed on a Varian Cary 50 spectrometer, the CD spectra on a Jasco J800 spectrometer equipped with a temperature control unit, infrared with the Bruker Tensor 27 FT-IR and the Thermo LCQ advantage max, ESI, equipped with an autosampler was used for mass spectrometry measurements.
Chemicals. All chemicals were used as received, unless noted otherwise. Azobenzene **2**[1]and PMAz[2,3] were prepared following literature procedures. 5CB was kindly provided by Merck.

Compound 1. *N*-*tert*-Butoxycarbonyl-d-alanine (4.27 g, 22.6 mmol) and 3-bromo-1-aminopropane hydrobromide (2.83 g, 20.5 mmol) were dissolved in CH_2Cl_2 (150 mL). To this solution *N*,*N*-diisopropylethylamime (DIPEA, 2.91 g, 22.6 mmol), *N*-hydroxybenzotriazole (HOBT, 4.03 g, 23.6 mmol) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC, 3.50 g, 22.6 mmol) were added. After stirring for 24 hours, the solution was washed consecutively with an aqueous 10% (w/w) citric acid solution (2 x 100 mL), H_2O (100 mL), aqueous saturated sodium carbonate (2 x 100 mL), H_2O (100 mL) and brine (100 mL). The organic layer was dried over Na_2SO_4, concentrated and subjected to column chromatography (EtOAc/CH_2Cl_2 1:9), yielding 1 as an off-white solid (3.69 g, 58%). Analysis: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.43 (s, 1H, NHboc); 4.93

(s, 1H, NH-alkyl); 4.17 (q, *J* = 7.0 Hz, 1H, CH); 3.43 (t, *J* = 6.6 Hz, 2H, CH_2Br); 3.39 (m, 2H, CH_2NH); 2.08 (quin, *J* = 6.5 Hz, 2H, CH_2); 1.45 (s, 9H, *t*-Bu); 1.36 (d, *J* = 7.0 Hz, 2H, CH_3). MS-ESI m/z = 310 [M+H].

Compound 3. A solution of **3** (1.30 g, 4.20 mmol) in DMF (20 mL) was cooled to 0 °C and slowly potassium tert-butoxide (0.47 g, 4.20 mmol) was added. The colour of the reaction mixture changed from dark purple to a dark blue. Bromide **1** (1.41 g, 4.48 mol) was slowly introduced in the reaction mixture, the ice bath was removed and the mixture was allowed to reach room temperature. To complete the reaction, the mixture was stirred at 100 °C overnight. After cooling, the reaction mixture was washed with dilute aqueous HCl (0.1 M, 100 mL), saturated sodium bicarbonate (100 mL) and water (200 mL). The organic layer was dried over Na_2SO_4 concentrated and subjected to column chromatography (EtOAc/CH_2Cl_2 1:4), yielding **3** as a red solid (1.06 g, 46%). Analysis: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 9.1 Hz, 2H, CH aromatic); 7.84 (d, *J* = 9.1 Hz, 2H, CH aromatic); 7.80 (d, *J* = 9.4 Hz, 1H, CH aromatic); 6.60 (s, 1H, NHboc); 6.34 (dd, *J* = 9.4, 2.6 Hz, 1H, CH aromatic); 6.18 (d, *J* = 2.6 Hz, CH aromatic); 4.84 (s, 1H, NH-alkyl); 4.24 (t, *J* = 6.9 Hz, 2H, CH_2O); 4.00 (q, *J* = 7.1 Hz, 1H, CH alanine); 3.55 (m, 2H, CH_2NH); 3.46 (q, *J* = 7.1 Hz, 4H, CH_2N); 2.10 (quin, *J* = 5.9 Hz, 2H CH_2 spacer); 1.37 (s, 9H, *t*-Bu); 1.25 (t, *J* = 7.1 Hz, 6H, C*H*$_3$ azobenzene); 1.20 (d, *J* = 7.1 Hz, 3H, CH3 alanine). MS-ESI m/z = 543 [M+H].

Compound 4. The boc protecting group was removed by dissolving **3** (990 mg, 1.82 mmol) in a solution of HCl in ethyl acetate (2.3 M, 15 mL). The color of the reaction mixture changed from dark red to pale orange. After 5 hours stirring at room temperature, the reaction was quenched by the addition of aqueous NaOH (0.1 M, 100 mL). The organic phase was separated, washed with water (100 mL), dried over Na_2SO_4 and concentrated. The free amine was directed converted to the formamide by the addition of sodium formate (1.12 g, 16.5 mmol) and ethyl formate (30 mL) and heating the reaction mixture to reflux for 48 h. After cooling and removal of the solvent by evaporation, the crude product was subjected to coloumn chromatography (EtOAc/CH_2Cl_2 1:4) to yield **4** as a red solid (789 mg, 80 %). Analysis: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 9.1 Hz, 2H, CH aromatic); 8.01 (s, 1H, CHO); 7.84 (d, *J* = 9.1 Hz, 2H, CH aromatic); 7.81 (d, *J* = 9.4 Hz, 1H, CH aromatic); 6.31 (dd, *J* = 9.4, 2.6 Hz, 1H, CH aromatic); 6.19 (d, *J* = 2.6 Hz, CH aromatic); 6.10 (s, 1H, NH formamide); 4.84 (s, 1H, NH-alkyl); 4.28 (t, *J* = 6.9 Hz, 2H, CH_2O); 4.20 (q, *J* = 7.1 Hz, 1H, CH alanine); 3.59 (m, 2H, CH_2NH); 3.48 (q, *J* = 7.1 Hz, 4H, CH_2N); 2.16 (quin, *J* = 6.9 Hz, 2H CH_2 spacer); 1.27 (t, *J* = 7.1 Hz, 6H, C*H*$_3$ azobenzene); 1.15 (d, *J* = 7.0 Hz, 3H, CH_3 alanine). MS-ESI m/z = 471 [M+H].

Compound 5. A mixture of **4** (750 mg, 1.59 mmol) and methyl *N*-(triethylammoniumsulfonyl)carbamate (Burgess' reagent, 0.70 mg, 2.90 mmol) in CH_2Cl_2 was refluxed for 5 hours. After cooling, the reaction mixture was concentrated and the crude product subjected to column chromatography (acetone/CH_2Cl_2 4:96) to give the isocyanide monomer **5** as a

red solid (675 mg, 82 %) that was stored until polymerization reaction at –20 °C. Analysis: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 7.9 Hz, 2H, CH aromatic); 7.86 (d, *J* = 8.0 Hz, 2H, CH aromatic); 7.83 (d, *J* = 9.4 Hz, 1H, CH aromatic); 6.38 (dd, *J* = 9.4, 1.5 Hz, 1H, CH aromatic); 6.22 (d, *J* = 1.6 Hz, CH aromatic); 4.31 (t, *J* = 6.3 Hz, 2H, CH_2O); 4.05 (q, *J* = 7.0 Hz, 1H, CH alanine); 3.64 (m, 2H, CH_2NH); 3.52 (q, *J* = 7.0 Hz, 4H, CH_2N); 2.17 (quin, *J* = 6.7 Hz, 2H CH_2 spacer); 1.51 (d, *J* = 7.0 Hz, 3H, CH_3 alanine); 1.27 (t, *J* = 7.0 Hz, 6H, CH_3 azobenzene). MS-ESI m/z = 471 [M+H]. FT-IR (cm^{-1}, ATR): 3296, 3100 (NH); 2141 (C≡N); 1666 (C=O); 1513, 1369 (NO_2); 1214 (tert. amine). UV-vis (EtOH): λ_{max} = 500 nm.

The maximum solubility of **5** in 5CB was determined by sonicating an excess of **5** in 5CB for 10 minutes and filtering the suspension through a microfilter (0.2 µm pores). The filtrate was diluted 1000 fold with chloroform and the concentration 5 in the solution was determined spectroscopically. The maximum solubility of 5 in 5CB is 0.064 wt-%, but to ensure full solubility of the monomer, default reactions were carried out at a slightly lower concentration of 0.035 wt-%.

Polymerization of 5 in chloroform

A round bottom flask (10 mL) was charged with isocyanide monomer **5** (14.0 mg) and distilled chloroform (1.0 mL). The initiator/catalyst solution (200 µL) was added and the progress of the reaction was followed by TLC and IR, UV-vis and CD spectroscopy. After full consumption of **5** (monitored by IR spectroscopy), diisopropyl ether (10 mL) was added and the polymer was centrifuged (3000 rpm, 5 min). The clear solvent was decanted and the solids were washed twice more with diisopropyl ether (10 mL) and with intermediate centrifugation steps. After purification, CH_2Cl_2 (20 mL) was added to prevent the polymer from drying in.

Patterned AzoPIC alignment, switching and analysis

Polymerization of 5 in 5CB

Monomer **5** was dissolved in 5CB and stirred for a few days to ensure complete dissolution. Nickel(ii)perchlorate was dissolved in ethanol (1 mL) and afterwards dry toluene (49 mL) was added. Using a micropipette, a small amount was added to the **5**/5CB solution (1:500 catalyst/**5** ratio). After swirling for a short time, rubbed polyimide and photoaligned PMAz cells were filled with a drop of the solution at room temperature through capillary force. (Polarized) optical microscopy was used to investigate the polymerization of **5** and subsequent alignment in the anistropic cells. The remainder of the bulk solution was used for the spectroscopic analysis (UV-vis, CD).

Polyimide & PMAz cell fabrication

The fabrication of rubbed polyimide and photoaligned PMAz cells (including the photoalignment process) has been described in previous work[3] except that the cells were not completely sealed with epoxy glue.

Electric field application

Two electrodes were connected to the PMAz cell, which was placed in a custom designed cell holder on the x-y stage of the (P)OM. A function generator (HAMEG HM8130) was used to apply the electric field (continuous wave, 20 V, 1 V μm^{-1}, 1 MHz) to the LC template.

Cell opening

The glass cells were opened by soaking them in dichloromethane for 30 to 45 minutes. After this period, the softened epoxy glue was peeled of the glass by using a scalpel. The glass cells were pried open and the LC was removed by adding several drops of diisopropylether on the glass plates, which were removed after 15 minutes by tilting the glass plate on a piece of KimWipe.

(Polarized) optical microscopy

(P)OM images in Figure 3, 4, S5 and S6 were taken with a Leica DM-RX polarized optical microscope and a Leica DMC2900.
(P)OM images in Figure 5 and S3 were taken with a Olympus BX60 polarized optical microscope and a CoolSNAP-Pro camera. For determining the orientation of the 5CB mesogens, a 530 nm retardation plate was used.
(P)OM images in Figure 6 and S4 were taken with a Carl Zeiss Jenaval polarized optical microscope and an AmScope MD900E camera.

Additional instruments

Electron microscopy

For SEM imaging, samples were coated with gold/paladium using a Cressington 208HR sputter coater at 20mA for 10 seconds. SEM images were taken on a JEOL 6330 Cryo Field Emission Scanning Electron Microscope at 3 keV.

UV-vis & CD spectroscopy

The UV-vis spectra of **5** and **AzoPIC** (Figure 2) were taken with a Jasco V-630 and the CD spectra were taken with a Jasco J-815 spectrometer.

Polarized optical microscopy

Leica DM-RX polarized optical microscope and a Leica DMC2900.
Olympus BX60 polarized optical microscope and a CoolSNAP-Pro camera
Carl Zeiss Jenaval polarized optical microscope and an AmScope MD900E camera.

Figure S1. Infrared spectra of a polymerization reaction of **5** in chloroform (1 wt%). Prior to adding nickel-catalyst (1:5000), the isocyanide peak at 2141 cm^{-1} is prominently present (blue spectrum) but after addition over a couple of days it has completely disappeared (red spectrum), indicating a full conversion of **5** into **AzoPIC**.

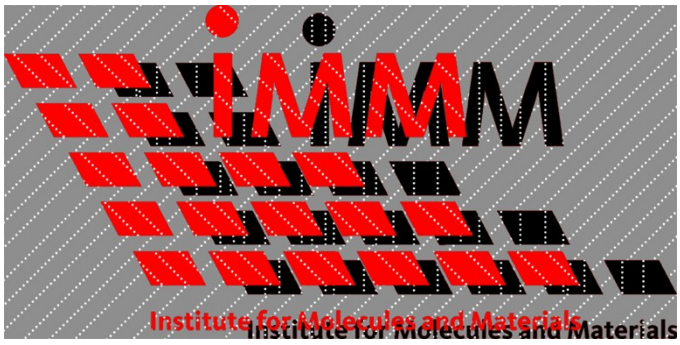

Figure S2. Schematic view showing how the CL depicted in Figure 3 was patterened in three orientations (indicated by black, grey and red colored domains). Lines within these domains indicate the orientation of the polarizer during photoalignment.

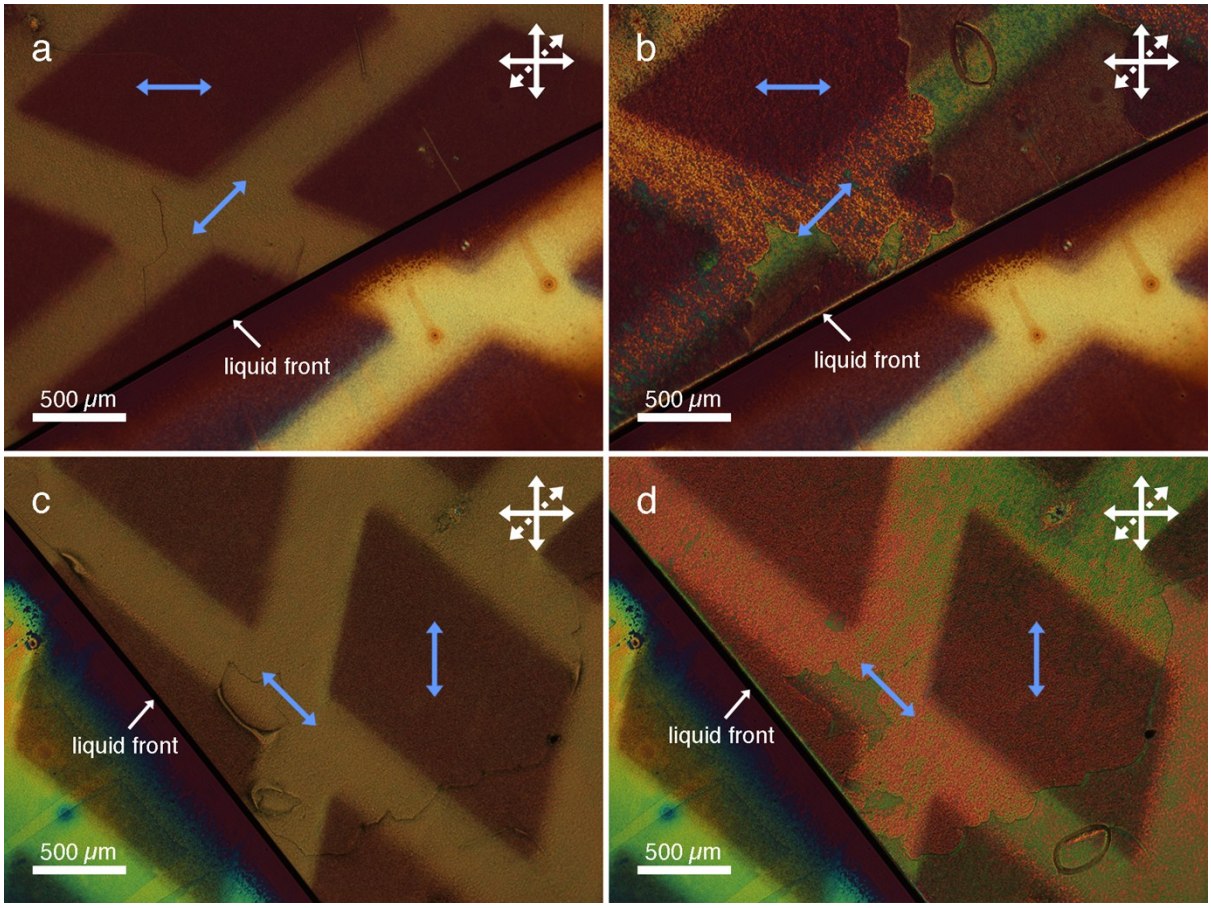

Figure S3. Determination of 5CB alignment with respect to PMAz. POM images with a 530 nm waveplate shows two domains of locally aligned 5CB (with **5** present), where the orientation of the linear polarized light used for the photoalignment is given by the light-blue arrows. Some pressure was applied to one side of the cell which increased the spacing of the glass plates on the other side, which caused a liquid front to move inside the cell. On the bottom right (a,b) and bottom left (c,d) part of images, there is a tiny layer of 5CB covering the insides of the PMAz coated plates, while the inside of the cell above the liquid front is fully filled with the 5CB solution. The layer thickness of the in-plane aligned bulk 5CB can also be drastically reduced bulk by applying a homeotropic electric field (b,d). The bulk LC reorients while a thin layer anchored strongly to the surface does not change its orientation. The thickness of the 5CB layer is related to the phase shift of the interference light. Since the layers below the liquid front are much thinner (also after applying an electric field in the domains above the liquid front), the phase shift is low enough to visual the difference in light color when a 530 nm wave plate is added. The phase shift decreases when the vector of the linear polarized of the photoalignment is parallel to the wave plate orientation (a,b) and increases when it is perpendicular to the vector of the light (c,d). This indicates that the azobenzene-moieties of the PMAz (which align perpendicular to the vector of the light) are parallel to the long axis of the 5CB mesogens.

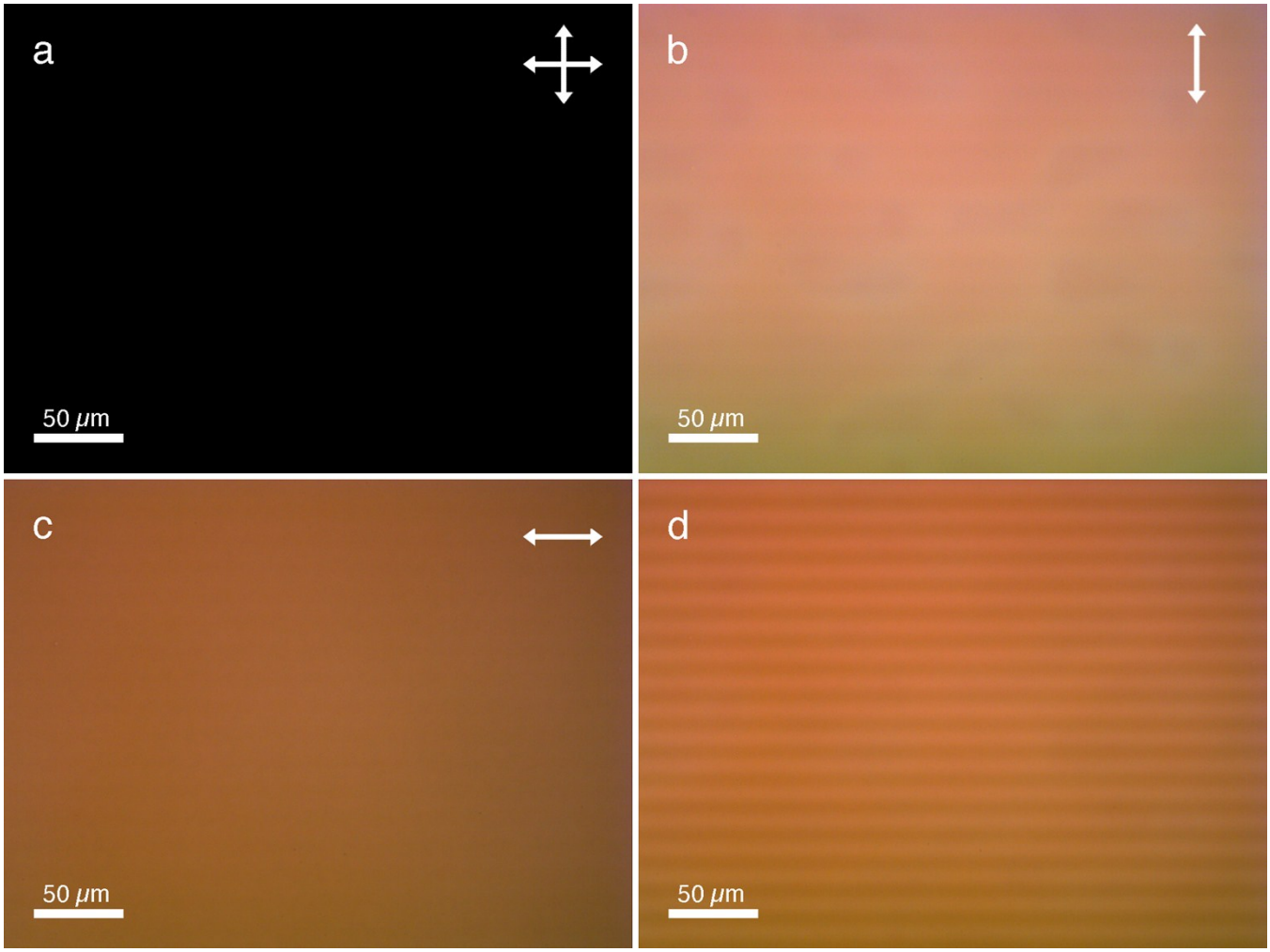

Figure S4. Microscopy images of **5** in 5CB (0.035 wt%) in a rubbed polyimide cell. No aligned red microscopic bundles of **AzoPIC** can be observed in the cell, where the polyimide is rubbed horizontally. Under cross polarizers parallel to the rubbing direction (a) no light is transmitted which indicates a completely aligned 5CB monodomain (parallel to the rubbing direction). Dissolved **5** (responsible for the red background) shows much less absorption when the polarizer is oriented perpendicular to the rubbing direction (b) compared to when the polarizer is oriented along the rubbing direction (c). OM image (d) shows the same image in absence of polarizers. The horizontal stripes in the background in image (d) are present due to interference of the light with the camera of the optical microscope.

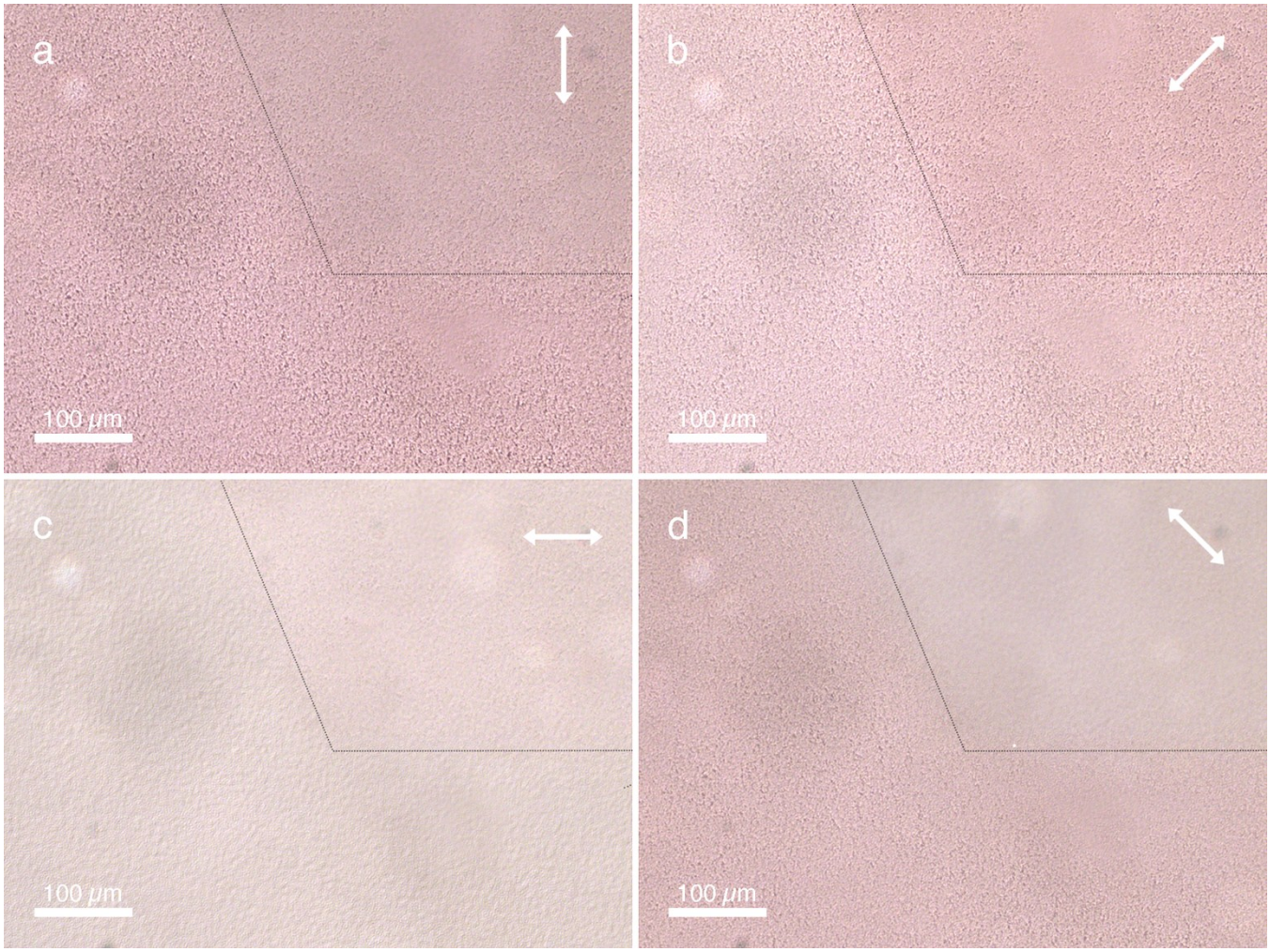

Figure S5. Microscopy images of **5** in 5CB (0.035 wt%) in photoaligned PMAz cell. No aligned red microscopic bundles of **AzoPIC** can be observed in the cell. Dissolved **5** (responsible for the red background) shows absorption characteristics when the polarizer (indicated by the double-sided white arrow) is oriented parallel to the photoaligned azobenzene mesogens of PMAz within one of the two domains. For visual clarity, the thin black line indicates the boundary between the photopatterned domains.

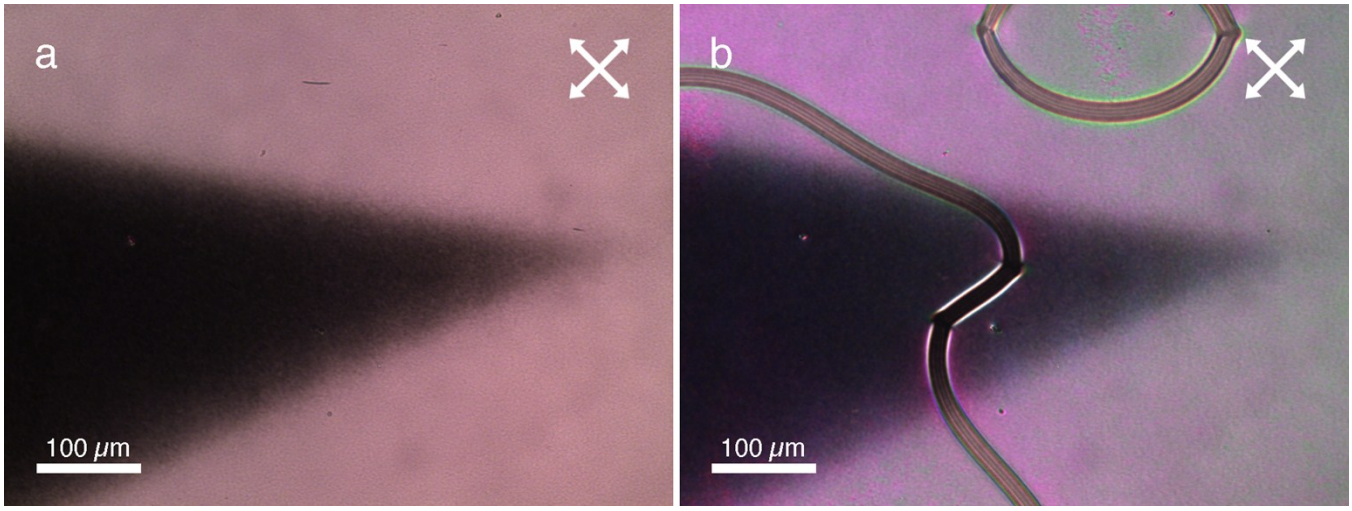

Figure S6. Polarized optical microscopy (POM) images of **AzoPIC** in 5CB (0.035 wt%) in photoaligned PMAz cell before (a) and during (b) application of electric field (20 V, 1 V μm^{-1} , 1 MHz). POM image (b) shows a purple color which is present due to a smaller phase shift of the light, indicating that the bulk LC has oriented homeotropically due to the electric field. A thin layer of 5CB has remained anchored to the PMAz surface, which is responsible for the observed birefringence. The thick stripes represent defect lines which appear after the application of the electric field, similar to those in Figure 5.

References

1 J. Griffiths and K. C. Feng, *J. Mater. Chem.*, 1999, **9**, 2333–2338.

2 M. Moniruzzaman, C. J. Sabey and G. F. Fernando, *Macromolecules*, 2004, **37**, 2572–2577.

3 P. van der Asdonk, H.C. Hendrikse, M.F.-C. Romera, D. Voerman, B.E.I. Ramakers, D.W.P.M. Löwik, R.P. Sijbesma, P.H.J. Kouwer, *Adv. Funct. Mater.* 2016, **26,** 2609-2616.