Direct mapping of local director field of nematic liquid crystals at the nanoscale

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Liquid crystals (LCs), owing to their anisotropy in molecular ordering, are of wide interest in both the display industry and soft matter as a route to more sophisticated optical objects, to direct phase separation, and to facilitate colloidal assemblies. However, it remains challenging to directly probe the molecular-scale organization of nonglassy nematic LC molecules without altering the LC directors. We design and synthesize a new type of nematic liquid crystal monomer (LCM) system with strong dipole–dipole interactions, resulting in a stable nematic phase and strong homeotropic anchoring on silica surfaces. Upon photopolymerization, the director field can be faithfully “locked,” allowing for direct visualization of the LC director field and defect structures by scanning electron microscopy (SEM) in real space with 100-nm resolution. Using this technique, we study the nematic textures in more complex LC/colloidal systems and calculate the extrapolation length of the LCM.

Significance

It has been challenging to directly probe the molecular-scale organization of nonglassy nematic liquid crystal (LC) molecules without altering the LC directors. Here, we design and synthesize a new type of stable nematic liquid crystal monomer (LCM) system with strong dipole–dipole interactions. The new LCMs can achieve faithful anchoring and alignment control at various boundaries, analogous to that of small molecule LCs. Upon photo-cross-linking, the orientational order of mesogens is effectively and faithfully locked, allowing for direct visualization of the LC director field and defect structures by scanning electron microscopy (SEM) with 100-nm resolution. Further, we use SEM imaging to calculate the extrapolation length of the LCM for planar and homeotropic anchoring.


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literature; this inherent obstacle becomes increasingly obvious under complex confinement.

To address this, we specially designed and synthesized a series of LCMs (LCM_X1, LCM_X2, and LCM_X3) (Figs. 1 and 2) with both strong surface anchoring and highly stable nematic phases. These LCMs suppress spurious defects, leaving only those required energetically and topologically. The monomers all have the same aromatic ester-based mesogenic group, each common and inexpensive to synthesize, with an ortho-substituted nitro group but different terminal groups, epoxy and alkene, both of which are readily photo-cross-linkable at ambient conditions via photoacids and “click” chemistry, respectively. We confirmed the chemical structures via 1H-NMR (SI Appendix, Fig. S2). Similar LCMs terminated with epoxy or alkene groups have been reported with nematic phases in the literature (30) although they typically have very high phase transition temperatures, making it difficult to maintain the director field during polymerization due to the relatively low viscosity of the LCMs in the nematic phase. In addition, their anchoring properties have not been well characterized.

We introduced a pendant nitro group on the aromatic ring because it has been suggested that (i) LCs with a nitro group at the ortho position to a linkage ester group typically form a nematic phase with a relatively low phase transition temperature (31) and, more importantly, (ii) the introduction of a polar (e.g., nitro) or polarizable group into the chemical structure often results in an increase of molecular polarity, affecting molecular packing and, in turn, the phase stability of LCs (31). In particular, aromatic esters are well-known to achieve a stable nematic phase through strong intermolecular dipole–dipole interactions between carbonyl groups of adjacent molecules, an effect that increases with the strength of the molecular interaction (32, 33). In our system, we expect strong dipole–dipole interactions between carbonyl groups (dipole moment μ = 2.4D) (34) that are evenly distributed along the molecule and a more polar nitro group (μ = 4.01D) (34) in the middle of the molecule. Because each nitro group bonds randomly to one of the four sites from the adjacent LC molecule, crystallization is suppressed, as seen in analogous systems (30, 33, 35), leading to a highly stable nematic phase (SI Appendix, Fig. S3 and Movie S1) with strong surface anchoring properties for all LCMs we synthesized (Fig. 3 A–C and SI Appendix, Fig. S4). Here, we focused our study on LCM_X1 both because it has a large nematic window (>100 K) with the nematic phase starting slightly above its glass transition temperature (~10 °C) and because the terminal epoxy groups could be rapidly and locally cross-linked by photocids without large volume change—effectively locking the orientational order of mesogens for later SEM imaging.

We used patterned substrates that were well characterized in our laboratories, including membranes with cylindrical pores, micropillar arrays, and square-shaped one-dimensional (1D) microchannels with strong homeotropic anchoring (details in Materials and Methods) to study the alignment of newly synthesized LCMs in comparison with small molecule NLC, 5CB. As seen from the polarized optical microscopy (POM) and bright-field (BF) images shown in Fig. 3 A–C, both molecules are readily aligned with nearly identical director configurations on all patterned substrates despite the difference in surface treatments to align LCM_X1 vs. 5CB. For LCM_X1, homeotropic anchoring was achieved on silica-coated surfaces whereas planar anchoring was achieved on polyimide-treated surfaces (SI Appendix, Fig. S6). This is in sharp contrast to the behavior of commonly used LCMs, RM257 and LCM_AZO, which exhibit polydomains on the same substrates regardless of surface treatment (SI Appendix, Fig. S1). Note that the anchoring behavior of LCM_X1 shown in SI Appendix, Fig. S6 is visualized from SEM images of its LCP. As we discuss later, the LC director is maintained from LCM to LCP.

In cylindrical pores with homeotropic anchoring on all boundaries, the nematic director either forms a bulk point defect with integer topological charge (±1) in the center or “escapes into the third dimension” (36, 37) to separate two half-defects on the boundaries. Likewise, in the pillar arrays, there could be a bulk disclination ring surrounding the pillars (15) or an escape configuration where the defects are all concentrated next to the pillar edges. However, neither POM nor BF microscopy can distinguish these two modalities without further investigation of the director field through the whole sample or through the use of a variety of state-of-the-art tools such as confocal polarized microscopy.

To access the director information in these geometries, we cross-linked the LCMs through cationic polymerization of epoxies, a common reaction in negative-tone photoresists (38, 39). Compared with acrylate and methacrylate groups that are often used in radical polymerization of LCMs, epoxides have several advantages that are key to our LCM design: (i) They are insensitive to ambient oxygen. (ii) They can be cross-linked efficiently through chemically amplified ring-opening reactions; each photogenerated acid can initiate hundreds of reactions locally, rendering fast polymerization without large volume shrinkage seen in (meth)acrylate polymers. (iii) The bulky aromatic ester mesogens limit acid diffusion at room temperature; therefore,
photopolymerization occurs locally. Together with the strong dipole–dipole intermolecular interactions, our LC molecules can lock in position effectively without altering the field direction during polymerization. Closely related are earlier studies of cationic photopolymerization of LC diepoxides (40, 41), which show that the NLC phase is maintained in the densely cross-linked network—in contrast to that from radical polymerization of diacylates. It was noted, however, that unintentional heating by the high-intensity UV light could realign the mesogens, thus increasing the order parameter after curing (41). To prepare even clearer data, we further suppressed reorientation during cross-linking by performing the UV curing at room temperature (−25 °C) with a low UV light intensity (2 mW/cm²), keeping the viscous timescales longer than the polymerization timescale (details in Materials and Methods).

From the birefringence of the material (Materials and Methods) and the POM images of samples before and after polymerization (Fig. 3 D and E and SI Appendix, Fig. S7), we confirmed that on the micrometer scale the director field was preserved during polymerization. Once polymerized, we could use SEM to directly visualize the nematic texture with nanoscale resolution of the director configuration in various cross-sections obtained by fracturing the sample at room temperature. As shown in Fig. 4 A–C and SI Appendix, Figs. S6 and S8, the local director field is visible under SEM, represented by the nanofiber-like fracture structures, the footprints of the director field. We note that the polymer itself does not form fibers. Rather, the oriented structures observed in SEM are a consequence of the anisotropic mechanical properties of LCPs, in which the bulk elastic modulus is usually much smaller perpendicular to the director (21, 42) and in which fractures occur along surfaces parallel to the director field (43, 44). The same type of fracture pattern can be observed in a nematic polymer that has some similarity with our LCPs (42). Following the fracture structures, we directly mapped the LC alignment with 100-nm resolution as illustrated by the red dotted line in Fig. 4 A–C. From Fig. 4 A we determine the angle of molecular alignment at the surface to be 90° inside a wide channel; likewise, we can see that homeotropic anchoring breaks down when the director field is tightly confined as shown in Fig. 4 B and C. We can now directly visualize the defect structure in pores, pillar arrays, and 1D channels and observe that the director most often adopts an escaped configuration, avoiding defects in the bulk. By contrast, in POM the observed point- and line-like structures could just as well be the sign of a distorted director field or a defect. Further, from SEM images we can estimate the extrapolation length of the LCM (45) for planar and homeotropic anchoring (details in SI Appendix). We can estimate the elastic constant, which is on the order of a few pico- Newtons, in line with the elastic moduli of other LCPs.

Armed with our careful study of the local director field of LCs on patterned surfaces, we turned to more complex director field structures: point defects and line defects created by colloids with homeotropic anchoring suspended in NLC. POM images in Fig. 5 depict typical pictures of hedgehog and Saturn ring defects surrounding silica colloids. Although numerous studies have focused on these defects in LC systems with varying colloidal size, geometry, and topology (46–49), direct visualization of the director structure is difficult, as is measuring the precise position of the induced topological defects. With fracture and SEM, here, we can determine these features with 100-nm accuracy. Consider, for example, the hedgehog in Fig. 5 A; the defect can be seen as clearly located 2 μm above the colloid. In the same sample, we also found Saturn ring line defects around other silica colloids—Fig. 5 B shows a typical defect with a slightly tilted director field. This slight tilting (tilting angle <15°) could not be detected by POM (Fig. 5 B, Insets); however, it can be easily read from SEM.

We can use this technique to study the nematic textures in more complex LC systems. For instance, in Fig. 6 we show a LC cell treated for homeotropic alignment that we expect to image as black in POM. Instead, we see the appearance of blue regions, suggesting planar alignment, separated from the dark regions by disclination lines. Although such disclination lines are metastable in a neat NLC and relax very quickly, they can have a much longer lifetime when they are stabilized by colloids trapped at the disclinations. To observe the structures in Fig. 6 B–E with SEM, we again cooled down the sample and then cross-linked the LCM_X1. In Fig. 6 B a disclination line generated at the boundary of the homeotropic and planar regions is shown. The disclination line can be identified by the fracture structure below and above the fracture plane in SEM as shown in Fig. 6 B because of the different mechanical properties of the defect. Similar line defects can also be found in Fig. 6 C and SI Appendix, Fig. S9, where silica colloids are trapped at the boundary. From the SEM images, we can observe the merging of the line defect in the bulk of LC and the Saturn ring surrounding the colloid. Further, it should be noted that bulk disclinations can also be stabilized by pinning to boundaries of the LC cell, as illustrated in Fig. 6 D. The direct, clear visualization of the bending of the director field is useful to study the bending energy of LCs in various settings. Fig. 6 E shows the LC orientation inside a planar-like region stabilized by silica colloids. The escaped configuration is surprising because it requires a large bending of the director field from the homeotropic boundaries to the center of...
the LC cell, resulting in a high elastic energy in the bulk of this 2D LC thin film (~8 μm). A clarifying example of this behavior can be found in SI Appendix, where we show a SEM image of a small escape region whose boundaries could be both visualized in the same picture (SI Appendix, Fig. S10). The SEM images provide us a detailed director configuration in this small region, where the planar region starts at the surface of a colloid with an associated defect with charge −1, escapes in the direction determined by the defect structure around the colloid, and finally ends at another colloidal surface. These SEM studies thus provide us the capability to fully explore LC anchoring behaviors inside LC cells featuring complex topology and also to “lock” and observe metastable states.

In conclusion, we designed and synthesized a new LCM system with strong dipole–dipole interactions, resulting in a stable nematic phase and precise control of molecular anchoring and alignment on different boundary conditions. The director field can be faithfully “locked” by photo-cross-linking, allowing for direct mapping of the LC director field and defect structures by SEM. In turn, we can calculate the extrapolation length and estimate the elastic and anchoring constants of LCs (see SI Appendix for detailed discussion and SI Appendix, Figs. S11 and S12). This molecular design strategy can be extended to other substituents (e.g., to induce hydrogen bonding) and bridging groups that connect the mesogen and epoxy group to fine-tune the mesomorphic properties. Moreover, our LC monomers are low cost; e.g., LCM_X1 can be produced at a cost of ~10% that of 5CB, but with equal flexibility to be aligned on various boundary conditions. This newfound ability provides us with tools to enhance our understanding of anchoring, defects, and elasticity of short-molecule nematics, which will enable the further control of bulk structures via nanoscale patterning of the substrate and surface chemistry. We anticipate that by directly photopatterning a 2D sheet of NLC elastomer or glass with embedded defects and elasticity, followed by actuation by heat or light, we could induce folding into 3D.

Materials and Methods

Materials. All chemicals were used without further purification. Dime-thylformamide (DMF), dichloromethane (DCM), potassium hydroxide (KOH), sodium thiosulfate pentahydrate, and hydrochloric acid (HCl) were purchased from Fisher Scientific. Thionyl chloride (SOCl₂), 4-dimethylaminopyridine (DMAP), 2-nitrotetraphenolic acid, 4-hydroxybenzoic acid, metachloroperoxybenzoic acid (MCPBA), (3 Amino- propyl) triethoxysilane (APTES), allyl alcohol and (2- nitroterephthalic acid, 4-hydroxybenzoic acid, metachloroperoxy- benzoic acid (2). A total of 3.45 g 4-hydroxybenzoic acid (25 mmol) was gradually dissolved into 2.8 g KOH (50 mmol) aqueous solution (100 mL) and the solution was cooled in an ice water bath. A total of 2.48 g of (3) (10 mmol) was dissolved in 15 mL ethyl acetate and added dropwise into the above prepared aqueous solution under vigorous stirring. After 30 min, the reaction was stopped and the mixture was neutralized by diluted HCl (5 vol%) aqueous solution to pH 7. The resulting precipitate was then filtered off by vacuum filtration and washed with ethanol to obtain 4.28 g of product (2) (9.5 mmol, 95% yield) as a white solid. 1H-NMR (360 MHz, DMSO-d6): δ (ppm) = 7.41 (m, 4H, ArH of d), 8.02 (m, 4H, ArH of e), 8.36 (d, 1H, ArH of c), 8.65 (d, 1H, ArH of b), 8.79 (s, 1H, ArH of a).

2-Nitro, 1,4-benzenedicarboxylic acid, 1,4-bis[(2-chlorocarbonyl)phenyl] ester (3). A total of 4.06 g of (2) (9 mmol) was mixed with 15 mL thionyl chloride under stirring. Two drops of DMF were added as catalyst. The mixture was heated to 75 °C, and refluxed until no bubbles were generated from the solution. The reaction mixture was then cooled down to room temperature, and excess thionyl chloride was removed in vacuo. The crude product (3) was obtained as a white solid and used in the next step without further purification.

2-Nitro, 1,4-benzenedicarboxylic acid, 1,4-bis[4-(2-oxiranmethoxy)carbonyl]phenyl] ester (4, LCM_X1). A total of 1.3 g (−)-glycidol (17.6 mmol) and 3.90 g of (3) (8 mmol) were dissolved in 30 mL DCM, and the solution was cooled in an ice water bath at 0 °C. A total of 2.15 g DMAP (17.6 mmol) in 20 mL DCM was added dropwise into the above prepared solution under stirring. The reaction mixture was then gradually warmed up to room temperature and kept for another 6 h. The completion of the reaction was monitored with TLC until the reactant (3) was completely consumed. The mixture was then filtered through a celite pad, and the solvent was removed in vacuo. The resulting oil was purified by column chromatography (silica gel; eluent: DCM/EtOAc 20:1) followed by ethyl acetate (20 vol%). DCM = 1.15 g (88% yield) was obtained. 1H-NMR (360 MHz, CDCl₃): δ (ppm) = 2.75 (dd, 2H, −(O)COCH₂CH₂O), 2.93 (dd, 2H, −(O)COCH₂CH₂O), 3.36 (m, 2H, −(O)COCH₂CH₂O), 4.20 (dd, 2H, −(O)COCH₂CH₂O), 4.71 (dd, 2H, −(O)COCH₂CH₂O), 7.38 (m, 4H, ArH of d), 8.04 (d, 1H, ArH of c), 8.20 (m, 4H, ArH of e), 8.59 (d, 1H, ArH of b), 8.88 (s, 1H, ArH of a).

2-Nitro, 1,4-benzenedicarboxylic acid, 1,4-bis[4-(2-propenyl-1-oxoxy)carbonyl]phenyl] ester (5, LCM_X2). A total of 1.02 g allyl alcohol (17.6 mmol) and 3.90 g of (3) (8 mmol) were dissolved in 30 mL DCM, and the solution was cooled in an ice water bath at 0 °C. A total of 2.15 g DMAP (17.6 mmol) in 20 mL DCM was added dropwise into the above prepared solution under stirring. The reaction mixture was then gradually warmed up to room temperature and kept for another 6 h. The completion of the reaction was monitored with TLC until the reactant (3) was completely consumed. The mixture was then filtered through a celite pad, and the solvent was removed in vacuo. The resulting oil was purified by column chromatography (silica gel; eluent: DCM, followed by ethyl acetate: DCM, 1:15 vol/vol; Rf = 0.75). The purified product (5) was kept at 0 °C. At a total of 2.15 g DMAP (17.6 mmol) in 20 mL DCM was added dropwise into the above prepared solution under stirring. The reaction mixture was then gradually warmed up to room temperature and kept for another 6 h. The completion of the reaction was monitored with TLC until the reactant (3) was completely consumed. The mixture was then filtered through a celite pad, and the solvent was removed in vacuo. The resulting oil was purified by column chromatography (silica gel; eluent: DCM, followed by ethyl acetate: DCM = 1:30 vol/vol) to obtain 2.83 g of (5) (66.5% yield) as a white solid. 1H-NMR (360 MHz, CDCl₃): δ (ppm) = 4.87 (dd, 4H, −(O)COCH₂CH₂O), 5.32 (d, 2H, −(O)COCH₂CH₂O), 7.41 (m, 4H, ArH of d), 8.02 (m, 4H, ArH of e), 8.36 (d, 1H, ArH of c), 8.65 (d, 1H, ArH of b), 8.79 (s, 1H, ArH of a).
Following the procedure reported in the literature (50), Dow Chemical) on glass slides, using poly(dimethylsiloxane) (PDMS) molds, place before use.

Photoacid generator (PAG) were dissolved in 10 g DCM and kept in a cool and dark filtered off and the resulting solution was washed twice with sodium thiosulfate pentahydrate aqueous solution and then washed twice with brine. The allowed to stir for additional 48 h. After reaction, the white precipitate was solution. The reaction mixture was then warmed up to room temperature and 30 mL DCM at 0 °C. A total of 3.31 g MCPBA (20 mmol) was gradually added to the 4-(4-(((Oxiran-2-yl)methoxy)carbonyl)phenyl) 1-(4-((allyloxy)carbonyl)phenyl) 2-nitro-

1H-NMR (360MHz, CDCl3): δ 1.87 (3H, s, CH), 4.20 (dd, 1H, ArH of d′), 7.73 (m, 4H, ArH of c′), 8.04 (d, 1H, ArH of d′), 8.20 (m, 4H, ArH of e′), 8.59 (d, 1H, ArH of b′), 8.88 (s, 1H, ArH of a′).

**Preparation of Liquid Crystal Monomer Solutions.** A total of 200 mg liquid crystal monomer (4, LCM_X1) and 4 mg iragrace 261 (2 wt%; Ciba Specialty Chemicals) as photoacid generator (PAG) were dissolved in 10 g DCM and kept in a cool and dark place before use.

**Fabrication of Patterned Substrates.** All of the patterned substrates were fabricated by replica molding from commercially available epoxy (D.E. 354; Dow Chemical) on glass slides, using poly(dimethylsiloxane) (PDMS) molds, following the procedure reported in the literature (50).

**Preparation of substrates with desired LC anchoring.**

i) Homeotropic anchoring of LCs on flat substrates, porous membranes, and square channels. The anchoring type of the LC (homeotropic or planar) largely depends on the surface energy of the interface (51).

ii) Strong homeotropic anchoring of LCM_X1 on micropillar arrays. To achieve high homeotropic anchoring energy on micropillar arrays, we first treated pillars based on step (i), followed by functionalization of the SiO2 surface with APTES. Due to the Michael-addition reactions between the amino groups in APTES and epoxy groups in LCM_X1, the newly formed surface anchored LCM_X1, where the mesogenic group were orientated perpendicularly to the interface. As a result, the interaction between the interface and LCM molecules was substantially increased, showing stronger homeotropic anchoring than the SiO2-coated surface. In detail, the sample consisting of the micropillar array was immersed in a solution of 1 vol% APTES in an ethanol/water mixture (90:10 vol/vol) for ~10 min and then rinsed with ethanol and DI water three times and dried by air gun. Finally, the sample was baked in a convection oven at 100 °C for 15 min to 1 h.

iii) Planar anchoring. To create planar anchoring for LCMs, a glass substrate was spin coated with a thin layer of polyimide from its xylene solution at 5,000 rpm (on spin coater WS-650hbz-23NPP-UD-3; Laurell) for 30 s, followed by baking at 130 °C for 20 min. A uniform planar anchoring sample was obtained by rubbing the polyimide-coated substrate with a velvet cloth.

**UV Cross-Linking.** To prevent the reorientation of the directors of LCM_X1 during photopolymerization, UV curing was carefully performed in three steps, including (i) samples were slowly cooled down at 1 °C/min to room temperature (~25 °C); (ii) samples were exposed to a low UV power (~2 mW/cm²) at 365 nm, Hg lamp, overnight; and (iii) after UV exposure, samples were slowly heated up to 100 °C at a ramping rate of 1 °C/min. The sample was then cooled down from 130 °C to the desired temperature (cooling rate not critical here) to align LC.

**Characterization.** Chemical structures of the synthesized chemicals were confirmed with 1H-NMR performed on a Bruker Advance DMX 360 (360 MHz) spectrometer at 25 °C and analyzed with TOPSPIN software. Thermal analysis of the synthesized LCMs was performed on a differential scanning calorimetry (DSC) Q2000 (TA Instruments). Samples were heated and cooled under nitrogen with a ramping rate of 10 °C/min for three cycles. Data from the second cycle were reported. Liquid crystal phases and alignments were observed under an Olympus BX61 motorized optical microscope with crossed polarizers, using CellSens software. Liquid crystal polymer samples were manually broken into pieces or cut with a razor blade. The cross-section was coated with a 4-nm iridium layer for SEM. Imaging was performed on a dual-beam FEI Strata DB 235 Focused Ion Beam (FIB)/SEM instrument with a 5-kV electron beam.

**Measurement of Refractive Index and Birefringence.** We used Snell’s law to estimate the refractive indexes of LCM_X1 by comparing the apparent thickness of the LC cell, Dcell, with the actual cell thickness without LC, D0, that is.

DnLC = Du/DLC. We prepared a uniform planar cell in the way same as described earlier. Dn and DLC were measured before and after LC was infiltrated, respectively. Accordingly, we obtained the extraordinary refractive index, nex = \frac{1}{n_C} ± 0.02 and the ordinary refractive index, n_o = \frac{1}{n_C} ± 0.02 of LC when the polarized light was parallel and perpendicular to the LC director, respectively. The birefringence of LCM X1 was estimated as \pm 0.17. We also estimated birefringence of LCM X1 from a wedge cell, using the Michael-Levy chart before and after UV curing, as 0.16 ± 0.02, in good agreement with that measured from optical microscopy. Again, the consistent birefringence before and after polymerization as shown in Fig. 3 D and E clearly indicates that polymerization did not affect the nematic order parameter.

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Movie S1. Flow of LCM_X1 between micropillars in real time. One of the cover glasses was patterned with epoxy pillar arrays (D = 10 μm, P = 20 μm, H = 9 μm) coated with silica to impose homeotropic anchoring on all boundaries. The temperature was kept at 90 °C. The flow was manually created by mechanically pressing the LC sample with tweezers.

Other Supporting Information Files

SI Appendix (PDF)
Supporting Information

Direct mapping of local director field of nematic liquid crystals at the nanoscale

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Fig. S1. POM images of LCM_AZO [4-ethoxy-4'-(6-acryloyloxyhexyloxy) azobenzene] and RM257 [(1,4-Bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene)] on various patterned epoxy substrates coated with different surface chemistry. (A) LCM_AZO in polyvinyl alcohol (PVA) coated square array of pores. (B) LCM_AZO between PVA coated square array of pillars. (C) LCM_AZO in dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride (DMOAP) coated square array of pores. (D) LCM_AZO between DMOAP coated square array of pillars. (E) RM257 in PVA coated square array of pores. (F) RM257 between PVA coated square array of pillars. (G) RM257 in DMOAP coated square array of pores. (H) RM257 between DMOAP coated square array of pillars. Scale bar applied to all figures: 20 µm.

Pores in A, C, E, and G: diameter: 10 µm, pitch: 15 µm, depth: 20 µm.
Pillar arrays in B, D, F, and H: diameter: 10 µm, pitch: 20 µm, height: 19 µm.
Samples were cooled slowly (1 °C/min) from isotropic phase (100 °C for LCM_AZO and 130 °C for RM257) to nematic phase (94 °C for LCM_AZO and 125 °C for RM257).

Since the surface energy of the boundary determines the anchoring behavior of liquid crystal molecules (homeotropic or planar), we prepared patterned surfaces with both high (PVA) and low (DMOAP) surface energy. However, as seen from Fig. S1, it is clear that both LCM_AZO and RM257 fail to align uniformly on patterned surfaces regardless of the surface energy of the coatings and surface geometry. They mostly show polydomains with disclination lines either in the bulk or pinned to the boundaries. Although this non-equilibrium alignment can be improved by carefully annealing the sample through the nematic-isotropic phase transition, it is non-trivial to achieve the ideal equilibrium state with monodomains.
Fig. S2. $^1$H-NMR spectrum of the liquid crystal monomers (A) LCM_X1; (B) LCM_X2; (C) LCM_X3. Chemical structure of each monomer can be found in the main text, Fig. 1, and the corresponding proton labels can be found in Fig. 2.
Fig. S3. DSC curves of the LCMs. (A) LCM_X1. A nematic phase from 6.5 °C to 132 °C (heating) and 136 °C to 15 °C (cooling), respectively, was observed. (B) LCM_X2. A nematic phase was only observed upon cooling from 101 °C to 57 °C*. (C) LCM_X3.
A nematic phase was shown from -9 °C to 72 °C (heating) and 77 °C to -4 °C (cooling), respectively. 
*: A small peak at ~ 67 °C was observed, which could be attributed to packing of the end alkene groups of LCM_X2, since the system was still in the nematic phase at 65 °C as verified by POM.

DSC curves in Fig. S3 show that LCM_X1 and X3 did not crystallize upon cooling while LCM_X2 presented crystallization spreading over a large temperature range (~ 57 °C to ~ 17 °C). It is clear that the crystallization of all LCM’s was suppressed since there are multiple bonding sites designed in our systems with strong intermolecular dipole interactions.
**Fig. S4.** POM images of various LCMs on patterned substrates with homeotropic anchoring at the boundaries. (A) LCM_X2 in the square array of pores. (B) LCM_X2 between the square array of pillars. (C) LCM_X3 in the square array of pores. Scale bars: 40 µm. Insets: POM images with higher magnification. Scale bars: 10 µm.

Pores in A&C: diameter: 10 µm, pitch: 15 µm, depth: 20 µm. Pillar arrays in (B): diameter: 10 µm, pitch: 20 µm, height: 19 µm. Samples were fast cooled (~20 °C/min) from isotropic phase (LCM_X2, 110 °C; LCM_X3, 85 °C) to nematic phase (LCM_X2, 90 °C; LCM_X3, 70 °C).

Fig. S4 clearly demonstrates that even without careful cooling, the samples achieved equilibrium quickly and formed organized anchoring configurations over the entire sample area.
**Fig. S5.** UV-Vis spectra of LCM_X1 before and after UV curing.

**Fig. S6.** SEM images of fracture structures of liquid crystal polymers (LCPs) in different LC cells. (A) A homeotropic cell. (B) A hybrid cell with homeotropic anchoring on the top, and uniform planar anchoring at the bottom (on a rubbed polyimide). Scale bars: 2 µm.
**Fig. S7.** Maintenance of LC director field during photopolymerization. (A-B) POM and bright field (BF) optical images of LCM_X1 and its polymer in pillar arrays (diameter: 10 \( \mu \)m, pitch: 20 \( \mu \)m, height: 9 \( \mu \)m) with homeotropic anchoring imposed at all surfaces before (A) and after (B) UV curing. Insets in A&B: BF images show possible bulk line defects. (C-D) POM images of silica colloids dispersed in LCM_X1 with homeotropic anchoring at all surfaces before (C) and after (D) UV curing. Scale bars: A-B, 20 \( \mu \)m; C-D, 10 \( \mu \)m.

**Fig. S8.** SEM images of LCP in a channel. Images were taken from three different positions in the sample. Scale bars: 10\( \mu \)m.
**Fig. S9.** Merging of the line defects. SEM image of bulk disclination stabilized by multiple colloids. Scale bar: 2 μm

**Fig. S10.** Escaping behavior of LCs in a planar-like region. SEM images of LCP inside a planar-like region in a homeotropic LC cell. (A) The fracture structure shows stabilization of disclination lines with silica colloids sitting at the two ends of the planar-like region, and the escaping behavior of LC director from right to left. (B-C) A close look at the director field surrounding the colloid. Scale bars: 5 μm
Estimation of the LC elastic constants

As a proof-of-concept, the elastic anisotropy of LC was estimated by looking at the SEM images (see Fig. S11) of the LCs homeotropically anchored on the walls of a cylindrical pore. The director here “escapes in the third dimension” through a splay/bend deformation. We look at the angle $\theta$, that the nematic director adopts at any point relative to the axis of the pore (see Fig. S11 inset), as a function of the radius $r$, which goes from the center of the pore to its walls. The results are plotted in Fig. S11. We find that the data points can be very satisfactorily fit by (2)

$$\theta(r) = 2\tan^{-1}(\alpha r / R_0)$$  \hspace{1cm} (1)

where $R_0$ is the width over which the escape takes place (the radius of the pore), and $\alpha$ is a parameter that depends on the anchoring angle of the director on the homeotropic wall. Specifically, $\alpha$ is equal to the cotangent of the anchoring angle $\phi_h$ at the homeotropic wall of the capillary divided by two. Eq. 1 is the theoretical prediction for the escape configuration in a cylindrical channel in the approximation of single elastic constant. It holds when the splay constant and the bend constant are equal.

There is no a priori reason why this should be true for our monomers. However, Fig. S11 shows a good agreement between the experimental data and the theoretical prediction, which suggests that the ratio between splay and bend constant for our monomers is close to one. As shown in the literature(3), elastic anisotropy would lead to deviations from this curve.

Fig. S11. Director angle as a function of the radial coordinate $r$. The points are calculated from the escape configuration shown in the inset (scale bar, 5 $\mu$m). The line is calculated from Eq. 1.

We do not get information about the twist elastic constant in this configuration, but the lack of twisted escape configuration (observed, for example, in phases with very low twist elastic constant), combined with the observed structure of the hedgehogs near
colloids, suggests that the twist elastic constant is of the same order of magnitude as the other two.

From Eq. 1 and the model proposed by Crawford et al. (2), we can also estimate the extrapolation length for homeotropic anchoring, i.e. the ratio between the elastic and the anchoring constant. The anchoring angle \( \varphi_h \) on the homeotropic wall is \( \varphi_h = \sin^{-1}\left(\frac{(\alpha_0 W_h + K_{24})}{K - 1}\right) \), where \( W_h \) is the homeotropic anchoring constant, \( K \) is the elastic constant (always in the one elastic constant approximation), and \( K_{24} \) is the saddle-splay constant. If we make the common approximation of neglecting \( K_{24} \), we obtain the extrapolation length \( \xi_h = K/W_h = 1.3 \mu \).

In order to estimate the extrapolation length in the case of weak planar anchoring, we use a hybrid wedge cell, with one glass untreated (for homeotropic anchoring) and the other one treated with rubbed polyimide. Following the method in the literature (4), we can estimate the extrapolation length by directly measuring the angles formed by the liquid crystals in a hybrid wedge cell with the homeotropic and the planar surfaces, and relating them as:

\[
2 \xi_h (\varphi_p - \varphi_h) = d \sin\left(2(\Phi_h - \varphi_h)\right) \\
2 \xi_p (\varphi_p - \varphi_h) = d \sin\left(2(\Phi_p - \varphi_p)\right)
\]

Here, the subscript \( p \) and \( h \) represent the planar and the homeotropic surfaces, respectively, \( d \) is the cell thickness, \( \xi \) the extrapolation length, \( \Phi \) the preferred angle with respect to the normal and the flat surface (that is, \( \Phi_h \) is zero and \( \Phi_p \) is \( \pi/2 \)), \( \varphi \) is the angle that the nematic director forms with the normal to the cell surface (see Fig. S12). In writing this formula from ref. (4), we already make the approximation that the ratio of the splay and bend elastic constant is close to unity. The extrapolation length can then be estimated at various thicknesses of the wedge cell. We could estimate \( \xi_h \) from the study of LCM in the pores with homeotropic anchoring, and that with planar anchoring, \( \xi_p \).

The preferred tilt angle on the planar polyimide surface could be independently estimated by measuring it directly from the SEM images on a planar cell. The points in the SEM image shown in Fig. S12 represent measurements of the extrapolation length at different thickness of the wedge cell, ranging from 6 \( \mu \) to 30 \( \mu \), which gives a value of the planar extrapolation length \( \sim 10 \mu \), i.e. ten times longer than the homeotropic extrapolation length. This clearly shows that the anchoring is weaker on the polyimide than on the silica surface.

We should remark that the direct visualization of the director profile by SEM image makes it extremely simple and direct to calculate the relevant parameters for our newly synthesized LC.
Fig. S12. SEM image of a hybrid wedge cell (left panel), with highlighted angles at the planar and homeotropic surface, and the corresponding measurements of the planar anchoring extrapolation length (right panel) taken from the cell at different cell thicknesses (indicated next to each data point, in microns). Scale bar in SEM image, 10 µm.

A crude estimate of the elastic constants can be obtained simply by dividing the energy necessary to align the mesogens (i.e. the thermal energy at the temperature at which the mesogen achieves its alignment, around 370K) by the molecular size $a$.

$$K = k_B T / a = 1.4 \times 10^{-23} \times 370 \text{ K} \times 0.5 \times 10^9 \text{ m}^{-1} = 2.6 \times 10^{-12} \text{ N.}$$

Consequently, the homeotropic anchoring constants can be calculated as the ratio between the elastic constant and the extrapolation length: $W_h = 2.6 \times 10^{-12} \text{ N} / 1.3 \mu\text{m}=2 \times 10^{-5} \text{ N/m}$ and $W_p= 2.6 \times 10^{-6} \text{ N/m}$.

Video S1 shows flow of LCM_X1 between micropillars in real time. One of the cover glasses was patterned with epoxy pillar arrays ($D = 10 \mu\text{m}, P = 20 \mu\text{m}, H=9 \mu\text{m}$) coated with silica to impose homeotropic anchoring on all boundaries. The temperature was kept at 90 °C. The flow was manually created by mechanically pressing the LC sample with tweezers.

Reference: