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Lithographic Alignment of Discotic Liquid Crystals: A New Time–Temperature Integrating Framework

By *Massimiliano Cavallini*,* *Annalisa Calò*, *Pablo Stoliar*, *Jean Crispin Kengne*, *Sandrine Martins*, *Francesco Cino Maticotta*, *Florence Quist*, *Gabin Gbabode*, *Nicolas Dumont*, *Yves H. Geerts*, and *Fabio Biscarini**

Liquid crystals (LCs) are a successful example of how the control of self-assembling^[1,2] and self-organization^[3] via chemical design^[4] leads to novel applications. These are mostly based on bulk (quasi-)equilibrium properties related to long-range molecular ordering and anisotropy. Here we present a new application of LCs based on local, non-equilibrium properties: a logic pattern, which is also able to record the thermal history of the system as a time–temperature integrator. The multifunctionality of discotic LCs (DLCs)^[5] is the result of lithographic control of the self-assembling.^[6] DLCs domains, whose alignment differs from that of the surrounding dominant phase, are patterned into a logic “checker-board” where each domain codes for one bit of a binary information. When the temperature overcomes the phase transition temperature T_{r-h} between columnar rectangular and hexagonal mesophases, the individual domains progressively reorient into the dominant phase and their information is erased. The time spent above T_{r-h} is monitored from the irreversible change of the local birefringence. Since T_{r-h} can be tuned by chemical design, a new application of non-equilibrium LC patterns as time–temperature integrators coupled to information storage media can be envisioned.

LCs are central to many industrial applications such as flat-panel displays, and lately have been extensively explored as active materials for organic field effect transistors,^[7] photovoltaics,^[1] sensors,^[8] holographic data storage,^[9] and others.^[10] Their technological success stems from the enhanced self-assembling properties, which allow the formation and control of a variety of molecularly-ordered bulk mesophases but also the creation of organized structures^[11] in low-dimensional mesoscopic and

nanoscale-sized environments.^[12] Among several classes of LCs, DLCs consist of columnar superstructures formed by stacking of disk-like molecules. Molecular structure (Fig. 1a) exhibits a rigid aromatic core and highly flexible external chains, which provide solubility and improve the rheology of liquid crystalline phases.^[13]

Different thermodynamic phases emerge from the spatial arrangement of columns. The frequently observed phases, including the DLC used in this work, are columnar rectangular

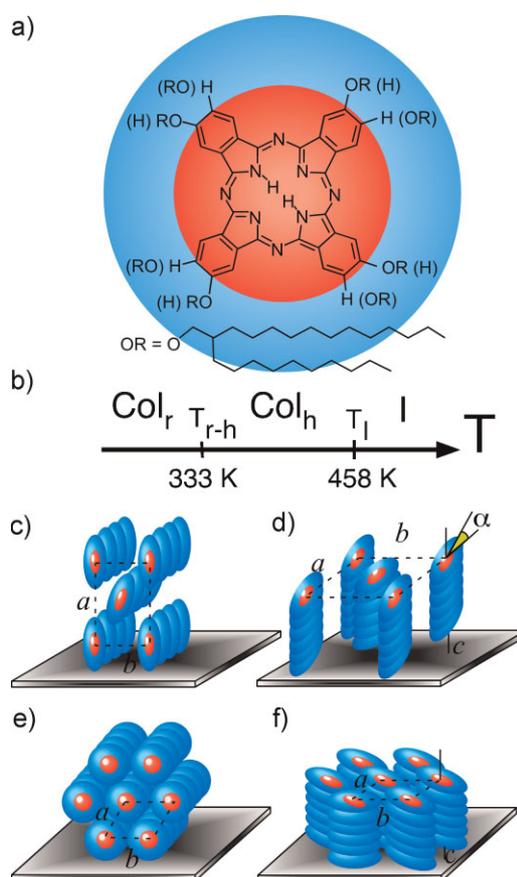


Figure 1. a) Chemical structure of our mesogenic phthalocyanine (Pc). b) Schematic phase diagram of Pc. Schemes of: c) rectangular planar columnar phase; planar alignment, d) rectangular columnar phase; pseudohomotropic alignment (n.b. the molecules are tilted with a certain degree α with respect to the surface), e) hexagonal planar, columnar phase; edge-on orientation, and f) hexagonal columnar phase; homeotropic orientation.

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(Col_r, see the schemes in Fig. 1c and d and the Supporting Information) columnar hexagonal (Col_h, see the schemes in Fig. 1e and f and the Supporting Information), and isotropic (I), with no long-range columnar order above a melting temperature T_1 . Remarkably, the transition temperatures can be tailored by the design of external chains of disk-like molecules.^[14]

Columns exhibit strong anisotropy in several properties, such as the electrical conductivity,^[10] optical properties,^[15] and exciton diffusion length^[16] along and perpendicular to the columns.

Here we have used a metal-free mesogenic phthalocyanine (Pc)^[17] whose structure is shown in Figure 1a. Pc is a prototypical DLC compound exhibiting a Col_r ↔ Col_h phase transition at $T_{r-h} = 333$ K and Col_h ↔ I at $T_1 = 458$ K. Pc films were cast from solution onto silicon wafers with native silicon oxide or glass substrates.

When deposited onto a surface the columns of DLC lie down (planar alignment) or stand up (perpendicular or homeotropic alignment) on the surface depending on the deposition process. In particular using Pc the planar alignment is spontaneously achieved when a film of DLC is deposited by drop or spin casting in air, regardless the nature of the surface (see X-ray diffraction in Supporting Information). It is usually more complex to obtain homeotropic (face-on) alignment, and several approaches have been proposed: photo-alignment;^[18] template growth;^[11] heat-quenching across the hexagonal-isotropic phase transition temperature T_1 , the material being confined between two surfaces.^[19,20] In the last case the process is very efficient and yields a quantitative homeotropic alignment. The alignment can be directly visualized using polarized optical microscopy (POM).^[21] Planar alignment results in a highly birefringent texture whereas homeotropic alignment, observed in Col_h phase, exhibits absence of texture (the image is dark due to the fact that the optical axis is equivalent to the columnar axis). Pc also presents another type of alignment, termed pseudo-homeotropic, which is observed for films confined between two substrates and corresponds to homeotropic alignment of a Col_r phase. Slightly birefringent textures are observed in this case due to the tilt that molecules present with respect to the column axis.

Here we locally modify the alignment of DLCs columns in the film by patterning the DLC film using lithographically controlled wetting (LCW),^[22] which is an unconventional lithographic method able to pattern nanostructures of functional materials starting from a liquid layer of their solution.^[23] Pc films (≈ 500 -nm-thick) were patterned by gently placing a stamp with recesses and protrusions on the film and without applying an external pressure, then by bringing the system to a temperature $T > T_1$ (schematics in Fig. 2a). In these conditions, for temperature $T_1 < T < T_1 + 10$ °C, the lateral confinement created by the stamp recesses prevents the thermal dewetting that is observed in films of Pc with a free exposed surface.^[24] In these regions, when the sample is cooled down to $T < T_1$ the columns retain their original planar alignment.

In the places where the stamp protrusions are in contact with the film, cooling down to T_1 leads the columns to achieve homeotropic alignment, which turns into pseudo-homeotropic below T_{r-h} . The process thus induces the formation of a specific column orientation at pre-set regions of the film, and a consequent spatial modulation of the tensorial properties associated to the local alignment of the columns. The result is shown in Figure 2.

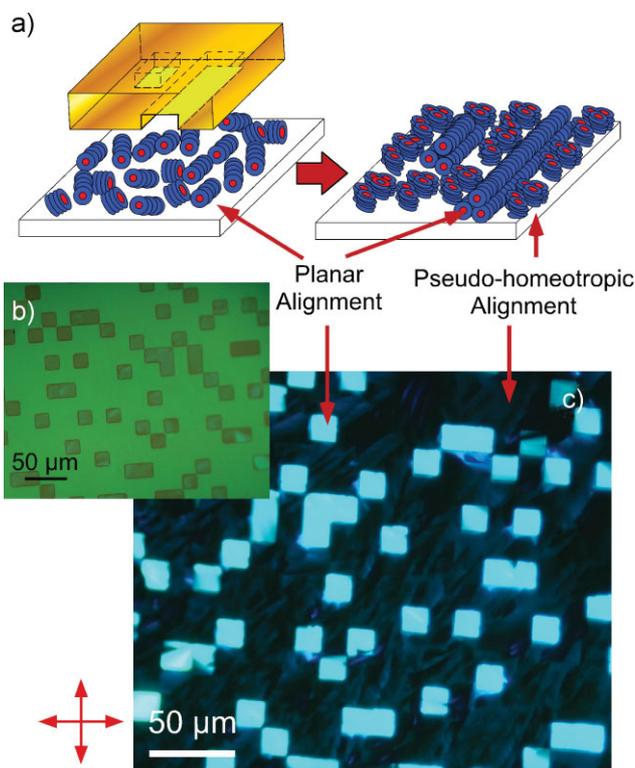


Figure 2. LCW induces a spatially controlled columns orientation in continuous thin films. a) Scheme of LCW applied on isotropic (fluid) phase. b) Optical microscopy images in bright field of the stamp and c) with cross polars of the patterned Pc film.

As a stamp we used a silicon oxide stamp containing a logic pattern coding binary information, where each non-zero bit is represented by a square hole 20 μm wide and 1.5 μm deep (Fig. 2b). The POM images of the patterned film (Fig. 2c) reveal that an array of domains of Pc replicating the stamp features was generated under these conditions. Each bit (corresponding to a recess of the stamp) is bright upon POM, revealing planar alignment of the columns inside. The homogeneous color contrast suggests that each bit completely corresponds to a planar aligned domain. The region surrounding the birefringent bits is slightly birefringent indicating that the columns are in pseudo-homeotropic alignment. In the patterned film spatially organized regions coexist (both corresponding at RT to the Col_r phase) with different local alignment with respect to the substrate. This result shows that it is possible to yield optically readable logic patterns by controlling the columns orientation within the continuous DLC film.

Patterned films are very stable and no effects of aging were observed while keeping the sample at ambient conditions for a few months. However the situation dramatically changes when the patterned film is heated up to the T_{r-h} transition. In this case, we observed a progressive reorientation of the columns within the bits from planar to pseudo-homeotropic. This behavior is partially counter-intuitive. In fact, when the film of Pc is cast in air, planar alignment of the columns dominates in both Col_r and Col_h phases.^[21] This indicates that the lithographical control can also be used to revert the minimum free energy alignment, leading to a metastable final state.

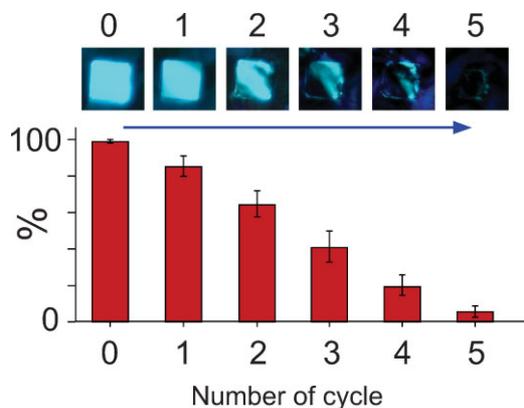


Figure 3. Evolution of the area of the birefringent zone observed by POM at room temperature inside a bit containing the planar aligned columns upon five thermal cycles around T_{r-h} . The graph shows the percentage of the area that lost birefringence.

The reorientation at T_{r-h} takes place within second time scale, and once the system returns to RT the changed features within the bits remain frozen. Thus, the reorientation is irreversible. By cycling the temperature from RT to T_{r-h} and back, the reorientation can be reiterated. The area of the zones changing phase increases proportionally to the number of thermal cycles. Figure 3 shows the evolution of a bit of Figure 2c, after several cycles from RT to 343 K using a heating (quenching) rate of $20\text{ }^{\circ}\text{C min}^{-1}$ waiting 5 min between each thermal cycle. In these conditions, $\sim 20\%$ of the squared bit area converts to homeotropic alignment during each thermal cycle. Thus, the irreversible transformation is able to record at least five thermal cycles.

Within a few tens of degrees above T_{r-h} , the fraction of bits changing the phase alignment does not depend on the absolute value of the temperature. Furthermore we observed columns reorientation only during the $\text{Col}_r \rightarrow \text{Col}_h$ transition. It is a matter of fact that maintaining the sample at $T > T_{r-h}$ no changes in the patterned films was observed by POM. The optical contrast shows that the reorientation starts at the boundary of the bit and then propagates inside the bit. This suggests that the process is driven by the need to decrease the extension of the boundary between the minority planarly-aligned columns and the majority homeotropically-aligned columns in order to produce a homogenous orientation. This phenomenology resembles coalescence or Ostwald ripening in LCs,^[25] where the smaller domains merge into the larger one with a progressive reorientation starting from the higher tension loci, viz. corners and line boundaries. Details about the mechanism of reorientation are currently under investigation.

This irreversible reorientation opens interesting perspectives for the DLCs because this phenomenon can be exploited to monitor the thermal history of the system. Such a device is termed a time (number of times)–temperature integrator. The plot in Figure 3 allows us to estimate the number of cycles from the fraction of bit surface that underwent the reorientation. As chemical design allows us to change T_{r-h} , a suitable array of patterned DLCs would record the thermal history across a tailored temperature range. To date, comparative TTIs exploit either chemical or biological reactions. Our approach is scalable down to domains with mesoscopic feature size (Fig. 3), which provides an

extra handle to tune the threshold temperature for the response, else to fabricate an array of temperature integrators.

In summary, we proved direct patterning of a continuous DLC film by the spatial control of columns orientation by LCW. We demonstrated that these patterned DLCs films can be used as time (number of times)–temperature integrators. The possibility to tune the T_{r-h} by tailoring the external chemical shape of the molecules, enlarges the application range of this class of materials. Here we used Pc as a representative material, but we observed a similar behavior in other DLCs^[26] thus this approach can easily be extended to other DLCs.

DLCs are interesting for several applications including photovoltaics, field-effect transistors, optoelectronics, and holographic information storage, where column orientation is crucial for the performance of the device. Patterning of DLC is not only suitable for enhancing the response of these devices, but as we showed can be used as a tool to endow the DLC film with a multifunctional response.

Experimental

The solutions of Pc (typically 1.0 g L^{-1}) were prepared in *n*-heptane (Spectroscopic grade quality). The substrates consist in a piece $10\text{ mm} \times 10\text{ mm}$ of commercial glass for optical microscopy and Si(110) wafer with native oxide. The substrates were cleaned using the standard protocol: sonication for 2 min in electronic-grade water ($18\text{ M}\Omega\text{ cm}^{-1}$), 2 min in acetone (Chromatography grade quality) then 2 min in 2-propanol (Spectroscopic grade quality). The stamps for printing were fabricated by conventional photolithography on silicon wafer. The motif (bits) consists of square holes $20\text{ }\mu\text{m}$ size and $2\text{ }\mu\text{m}$ deep, organized in a logical pattern containing a text in binary code. The films were prepared by drop casting $10\text{ }\mu\text{L}$ of the solution of Pc on the substrates in air. Before measurement, they were left 2 h at room temperature under nitrogen atmosphere in order to have a complete solvent evaporation. All the thermal treatments were done by commercial heating stage (Linkam THMS 600) under nitrogen atmosphere.

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