Dynamics of liquid crystal on hexagonal lattice

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Abstract
Nematic liquid crystal (LC) molecules adsorbed on two dimensional materials are aligned along the crystal directions of the hexagonal lattice. It was demonstrated that short electric pulses can reorient the aligned LC molecules in the preferred armchair direction of hexagonal boron nitride (h-BN). Several states with a variety of colors were obtained by changing the direction and strength of the electric pulses. The ab initio calculations based on density functional theory was carried out to determine the favorable adsorption configurations of the LC molecules on the h-BN surface. A non-volatile display, in which pixel resolution can be determined by grains of hexagonal surface, is proposed, which can offer a pathway towards dynamic high-quality pixels with low power consumption, and could define a new paradigm for all non-volatile display applications.

Introduction
The key aspect of liquid crystal (LC) based devices is the interaction of the LC molecules with a surface that provides a force for orientational alignment [1]. These molecules have preferred orientations which depend upon the surface morphology, chemical modifications, and the external electric field [2, 3]. The director alignment is a vital factor for controlling the features of displays, which on a smooth surface can be either planar or homeotropic configuration [2, 4]. LC molecules have a tendency to be aligned on rubbed polymer films [5], photo-polymerized structures [6], and patterned layers [7]. Most of these techniques for controlling the orientation utilize morphological surface anisotropy. The controllability of these treatments depends on the surface structure and molecular arrangement at the submicron scale. It is still challenging to realize molecular-level control of the nematic LC molecules.

As conventional nematic LC molecules have preferential orientation spontaneously [8, 9], an electric field should be applied to reorient them along the electric field against its preferential surface anchor-
such as graphene, hexagonal boron nitride (h-BN), and transition-metal dichalcogenides are visualized using the LC’s birefringence property [15, 16]. In the previous reports [12, 13], it was proposed that LC molecules tend to arrange along crystalline orientations of the 2D material owing to adsorptive interaction between the LC molecule and the hexagonal lattice [16, 17]. This technique was utilized to determine defects in graphene grown using chemical vapor deposition (CVD) during growth and transfer processes [18]. It is well-known that LC molecules tend to self-align into a helical structure with a small twist dependent on applied external force, which changes the polarization of propagating light along the helix exhibiting Bragg’s reflection [19].

In this paper, we report experimental and computational study of the flexibility of the alignment of LC molecules on 2D materials and proposed an innovative method to realize multistable states on a single grain of a hexagonal material. Taking the advantage of the insulating behavior of h-BN and hexagonal compatibility of LC molecules, alignment of LC molecules was tuned as a function of small DC voltage pulses. It has been demonstrated that small external force can re-orient the whole LC-domain along armchair directions. It was confirmed that several states with a variety of colors can be achieved by varying the combination of the electric field and the intensity of applied voltage pulses. It is believed that this approach can revolutionize the development of non-volatile and flexible displays, and also improve the utility of 2D nano-materials.

Methods

Synthesis of boron nitride (BN), graphene and MoS2
Hexagonal BN films were grown on Cu foil (Alfa Aesar, 99.8% pure, 25 μm thick) using a conventional thermal CVD mechanism (figure S1 (stacks.iop.org/TDM/5/045021/mmedia)). Mechanical and electrical polishing was applied to the Cu foil, and it was annealed at 990 °C for 30 min with H2 gas with 5 SCCM. After cleaning, h-BN was synthesized with borazine gas and hydrogen at 997 °C for 30 min. The furnace was cooled from 997 °C to 500 °C at a rate of ~35 °C min⁻¹. Ammonia borane (Sigma-Aldrich, 97% pure) was used as a precursor to form the h-BN film. The ammonia borane was thermally decomposed into hydrogen, aminoborane, and borazine at a temperature range from 80 °C to 120 °C. The h-BN films were transferred to secondary substrates, using a standard wet transfer method using poly methyl methacrylate (PMMA) (figure S3). Graphene was grown using a conventional CVD process with hydrogen and methane as carrier and precursor, respectively. MoS2 was grown using a two-step process- first, molybdenum was deposited using sputtering and second, CVD was employed in a sulfur environment to synthesize MoS2 films.

LC alignment
Commercially available nematic liquid crystal (5CB-Sigma Aldrich) was used. A 0.5 μl liquid crystal was spin coated (3000 rpm) for 60 s on CVD-grown boron nitride and graphene films in order to make the LC wet the surface. The liquid crystal molecules were directly aligned along the surface of the h-BN and domain orientation/boundaries can be observed under POM with cross polarizers. The sample was heated in order to reach thermal equilibrium of the LC anchoring interaction. First, it was observed at room temperature, and then the temperature was raised to 60 °C (higher than clearing point) for 15 min followed by cooling at ambient temperature. An LC cell was fabricated with a rubbed layer on the top electrode and polyvinyl alcohol (PVA) was spin coated on a glass slide. The film was uni-directionally rubbed and was placed over the LC-coated surface in order to confuse the anchoring orientation at the top layer. This gap was controlled by polystyrene beads to obtain a 1–2 μm thick LC cell.

Characterization

The LC alignment, boundaries and domain orientation were observed using a polarizer optical microscope (BX-51, Olympus Corp.). The axis of the polarizer was adjusted to be perpendicular to the analyzer. Raman spectroscopy with an excitation wavelength of 514 nm was used and power was kept below 1.0 mW to avoid laser-induced heating. The laser spot size of the Raman spectroscopy was 1 ± 0.2 μm. The AFM images were obtained in non-contact mode under ambient conditions using a commercial AFM (n-Tracer, NanoFocus Inc.).

Electro-optical measurements

Chrome masks were prepared with different types of electrodes. Optical lithography with a lift-off process was employed using a positive photoresist to pattern the electrodes on the silicon wafers. To investigate this electrical pulse response of aligned LC molecules, a digital signal generator was equipped with a digital-to-analog data acquisition interface card (National Instrument’s PCI Express 6353). National Instruments’ Data Measurement Services Software (NI-DAQmx) with LabVIEW was used to program pulse voltage sequences with a period of 2.5 ms. The voltage source unit and optical microscope image were synchronized by a PC program to allow correlated image analysis.

Computational details

Using density functional theory (DFT), we performed first-principles calculations to determine the favorable adsorption configurations of a 4-cyano-4′-pentylbiphenyl (C18H13N, also called 5CB) molecule and to study the atomic and electronic properties of them. We used the projector-augmented wave pseudopotential implemented in Vienna ab initio simulation package (VASP) code [20, 21] and a plane-wave basis set with the cut-off energy of 500 eV. For
exchange-correlation functional, the generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof [22] was employed. We also included the DFT-D2 method [23] for the van der Waals correction. The $6 \times 8$ h-BN supercell of an orthorhombic primitive cell was adopted as a substrate for liquid crystal molecules. In the primitive cell of h-BN, its optimized lattice parameters, a and b, were 4.35 Å and 2.51 Å, respectively. The lattice parameter, c, was chosen to be 24 Å. For the $6 \times 8$ supercell, the optimized lattice parameters, a and b, were 26.12 Å and 20.11 Å, respectively. Only the $\Gamma$-point was used in the $6 \times 8$ supercell calculation. All model systems were relaxed until residual forces acting on each atom were smaller than 0.02 eV Å$^{-1}$.

Results and discussion

Liquid crystal alignment

CVD-grown graphene and h-BN were transferred onto a silicon substrate using a conventional wet chemical route, whereas MoS$_2$ was directly grown on the silicon surface (see methods). LC (Sigma Aldrich-5CB) was spin coated to be 500 nm thick and heated above its isotropic temperature (60 °C), and allowed to cool at a slow rate of 1 °C min$^{-1}$ to minimize the effect of thermal flow [24]. Cooling leads to the alignment of molecules with a crystalline orientation of the hexagonal lattice structure. Figure 1(a) shows an optical microscope image of transferred h-BN without LC. A greenish color indicates the presence of h-BN and bluish color is ascribed to the oxide layer of the silicon. CVD-grown h-BN was characterized by atomic force microscopy (AFM) and Raman spectroscopy to estimate the quality and thickness of the transferred film (figure S2). Figure 1(b) shows a polarized optical microscopy (POM) image of LC coated h-BN with a cross-polarizer. Prominently, grains and boundaries of h-BN were the evidence of molecular alignment of nematic LC. Growth of the h-BN was improved by tuning the growth time, and the LC alignment was confirmed either on partially or completely grown h-BN (figure S3). The same technique was employed on graphene and molybdenum disulfide (MoS$_2$), and grains with clear boundaries were observed in all, as shown in figure 1(c). The versatility of this technique confirms its utility to different 2D nano-materials with hexagonal symmetry.

Our calculations determined the favorable adsorption configurations of a 5CB molecule on an h-BN sheet [20–23] (see methods). It was observed that h-BN has two different configurations with strong adsorption energy: armchair and zigzag directions with 120° rotation symmetry (figure S4). The computational simulations reveal that AB stacking of two phenyl rings on the 2D structure has the highest adsorption energy, compared with other possible alignment configurations (figure S5). As shown in figure 1(d), considering AB stacking, we chose atomic model structures of the 5CB molecule physisorbed on the h-BN sheet, rotating the adsorbate through 180°. Although two phenyl rings in a 5CB molecule have a relative angle of ~30°, the rings in this study are practically parallel to each other so as to maximize the van der Waals interaction with the h-BN sheet. Four armchair directions (0°, 60, 120, and 180°) and the three zigzag directions (30, 90, and 150°) was considered. Because of three-fold symmetry of h-BN, two structures with rotation angle difference of 120° correspond to an identical pair. All possible alignment states were observed and most stable states were depicted in figure 1(d) and S6. Consequently, the adsorption energies ($E_{\text{ad}}$) of the 5CB molecule, distance ($d$) between the 5CB molecule and h-BN sheet from the optimized atomic structures were derived. $E_{\text{ad}}$ is defined by

$$E_{\text{ad}} \equiv E_{\text{5CB}} + E_{\text{hBN}} - E_{\text{5CB+hBN}}. \quad (1)$$

Here, $E_{\text{5CB}}$, $E_{\text{hBN}}$ and $E_{\text{5CB+hBN}}$ are the total energies of free 5CB molecule, bare h-BN sheet, and a 5CB molecule adsorbed on h-BN sheet, respectively. The distance, $d$, was defined by the difference between the average height of the 5CB molecule and h-BN sheet. Adsorption energies of the 5CB adsorbates aligned in the armchair directions were 50–60 meV/molecule higher than those of zigzag direction. This energy gap can be considered an activation energy required for the 5CB molecule to rotate from one armchair direction to another. It was evident that there are three stable alignment states on a single grain, implying that LC molecules can be controlled into three possible directions by external sources. Earlier, we have suggested that the energy gaps were 25, 116 and 114 meV per molecule for graphene, MoSe$_2$, and WSe$_2$, respectively [25]. When two LC molecules were considered, including the interaction between them, a thermal excitation allows angle fluctuation, $\Delta \theta = \pm 14.9°$, but cannot rotate the molecules from one armchair direction to another (figure S9). When many 5CB molecules are adsorbed, it is expected to form a monolayer with directionally aligned state [26]. The anchored molecules may be aligned in a single-row or double-row type depending on length of alkyl chain [27]. Iwakabe et al. found that the single-row corresponds to the nematic phase in bulk structure, while the double-row corresponds to the smectic phase [27]. In either case, the orientation of the LC molecules is not changed during the transformation into the bulk state.

To manifest the correlation between the LC director and crystalline orientation of the surface, the molecular interaction was investigated in depth previously. It was observed that LC molecules can align on the six preferential states of the hexagonal surface, which was further confirmed theoretically [25]. It shows that the anchoring direction was determined mainly by the axis of two phenyl rings parallel to the armchair direction of the hexagonal lattice. To check the stability of the alignment of the LC molecules, thermal cycling test, above the phase transition temperature (figures
S11 and S12), was carried out. It was observed that the LC alignment directions were not completely the same as those before thermal treatment, indicating that the aligned direction of LC molecules can be changed by external conditions like temperature gradient, rather than determined by initial conditions like the geometry of the grains. The same alignment behavior was studied on bulk boron nitride flakes and interestingly, it was observed that LC can align on different orientation of single crystal h-BN (figure S13).

**LC-based display**

To physically investigate the idea of multi alignment on h-BN, three electrodes forming a triangle were fabricated to apply different field strengths and directions (figure S14). After fabrication of the electrodes, h-BN was transferred without using polymer to avoid possible residue on the surface. Detailed processes were discussed in supporting information (figure S15). LC was coated on the transferred film and the unidirectionally rubbed cover layer was placed on the LC (figure S16). Schematics of LC cell is shown in figure 2(a), where the rubbed layer was placed on LC to align one end of LC layer (LC-glass interface) parallel to the polarizer direction. Figure 2(b) shows the degeneracy of alignment of LC molecules on the 2D surface along three preferential directions. Depending on the preferential alignment angles at the 2D surface, LC molecules form twisted states.

h-BN was transferred in such a way that two grains were located between the electrodes. As shown in

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**Figure 1.** LC alignment on 2D nano-materials: CVD-grown 2D nano-materials were transferred to silicon. MoS2 was directly grown on silicon; LC was molecularly aligned with atomic orientation of 2D nano-materials (a) optical microscope image of transferred h-BN without LC, (b) POM with cross-polarizer image coated with LC. Noticeably, h-BN grains can be spotted and boundaries which were not visible without LC. (c) The same technique was applied to different 2D nano-materials (graphene and MoS2), and domains were observed in all. LC molecules have different alignment angle depending on the orientation of grown grains which eventually show different colors. (d) Computational results on adsorption distance, angle, and adsorption energy for each configuration of the LC molecule on h-BN. Alignment along armchair edges have the highest adsorption energy, and zig-zag alignments also have similar values. Energy difference between zig-zag and armchair edges is only ~50 meV per molecule and was shown in bottom right of (d). The distances between SCB molecule and h-BN sheet and adsorption energies are shown in legends.
A pulse with +10 V of 50 ms was applied to the electrode marked by ‘+’ in figure 2(d), while other two electrodes were grounded. Degenerate atomic compatibility of alignment on 2D surface assisted for LC to be twisted along one of the preferred orientations, which led to change red color of domain ‘a’ to blue. In figure 2(e), when field direction was changed by applying next pulse to other electrode, it also changed the color of domain ‘b’ from red to blue. When the third pulse was applied at the third electrode covering the two grains (‘a’ and ‘b’), both of them were turned blue (See supporting video). As a result, LC domain on each grain can be controlled independently using external local field from neighboring electrode, and the repeatability was confirmed by consecutive experiments. Stability of each state was confirmed for an hour as shown in figure S18. On the other hand, the gradation in color can be attributed to defects or impurities near the grain boundary, as well as the non-uniform thickness of the LC layer.

To confirm the versatility of this effect and to control the large area domain, two electrodes with different planar gaps were fabricated, as shown in figures 3(a)–(c). The LC layer thickness was adjusted to 1 μm with a rubbed layer, where the rubbing direction was indicated in blue arrows. DC pulses of 2.5 ms width with different polarities were applied. In figure 3(a), two grains were marked between electrodes with 10 μm spacing. When pulses of (10, –10 V) were applied on two electrodes, the grains 1 and 2 turned green. When polarity of the field was reversed (–10, 10 V) both the grains changed their color due to the opposite rotational twist of LC alignment. In order to revert back to the initial state, a vertical electric field (10 V) was applied using Si substrate, as shown in the last panel. Assuming most LC molecules were aligned nearly parallel to the rubbing direction initially, the LC alignment was tweeted by the pulses, as shown in the black arrows. When a pulse was applied from the left to the right electrode, LC directors near the h-BN surface were rotated +60° towards the other preferential state, causing the LC layer to be twisted. Similarly, when a field is applied from the right to the left, the LC directors were rotated –60° towards the third preferential state, causing twisting in the opposite direction. Interestingly, no color change was observed on the surface of the electrodes, which confirms the change was mainly dependent on the in-plane field between the electrodes.

Similar experiments were performed on the other samples having large grains, as shown in figures 3(b) and (c). In figure 3(b), two grains were marked between the electrodes with 50 μm gap, and the color of the 2nd grain was changed to blue (10, –10 V) and orange (–10, 10 V) depending on the field direction. The grain 1 did not show any significant change, which can be explained by the original alignment direction. If the LC on the grain were initially oriented in either 0 or 180° to the external field, no torque is applied and no change in color occurs. Similarly, in figure 3(c), the sample with large spacing (100 μm) also exhibited that the large domain of LC can be controlled and initialized in the same manner, even though there were some contaminations on the surface.

To understand the phenomena it is necessary to comprehend the dependency of transmittance on the
twist angle and the wavelength. It is well-known that a periodic modulation of the helical structure of cholesteric liquid crystals results in a selective reflection band, which is referred to as a photonic crystal. The pitch of the rotation of conventional cholesteric LC is dependent on chiral dopant of LC [28]. In case of the nematic LC, the twist is induced by the boundary surfaces, and its twisting rate is much lower than that of cholesteric LC. Gooch and Tarry suggested a model to estimate the transmission intensity for the arbitrary twist angles between the two alignment layers [29]. Transmission of the light propagating through twisted LC cell is given as:

\[ T = \frac{\sin^2 \left[ \frac{\theta \sqrt{1 + u^2}}{1 + u^2} \right]}{1 + u^2}. \]  

(2)

Where, \( u = \frac{n_d \Delta n}{\pi} \), \( \theta \) is the twist angle due to different alignment layers, \( d \) is the thickness of cell, \( \Delta n = n_e - n_o \) is refractive index difference of liquid crystal, and \( \lambda \) is the wavelength of light. In this model, the polarization direction was rotated parallel to the alignment direction. In this study, however, the polarization and analyzer were fixed perpendicular to each other, so Gooch–Tarry model should be modified. As LC molecules are aligned along armchair or zig–zag directions, \( \theta \) is independently varied. From Azzam’s model, when light propagates through the twisted LC, the ellipse of polarization, \( \psi \), was described as [30]:

\[ \psi(z) = Ve^{2i\theta z/d}. \]  

(3)

Here, \( e^{2i\theta z} \) represents periodic optical rotation, where \( z \) is propagating distance for the twisted LC cell located in \( x\text{-}y \) plane. The complex function, \( V \), describes the variation of the polarization ellipse in the space-rotating coordinate system [30]. If the incident light is linearly polarized in the \( x \)-direction, the output polarization at \( z = d \) is given as:

\[ \psi(z) = \frac{\sqrt{1 + u^2} - i(1 + u) \tan(\theta \sqrt{(1 + u^2)})}{\sqrt{1 + u^2} + i(1 - u) \tan(\theta \sqrt{(1 + u^2)})} e^{2i\theta}. \]  

(4)

In this experiment, the polarizer was fixed in \( x \)-axis, and the analyzer was in \( y \)-axis. Thus, the simplified general function of the transmittance can be obtained by taking imaginary parts (details in appendix):

\[ \text{Im}(\psi) = \frac{\sqrt{a^2 + c^2}}{\sqrt{a^2 + b^2}} \sin \left( \tan^{-1} \frac{c}{a} - \tan^{-1} \frac{b}{a} + 2\theta \right). \]  

(5)

Here, \( a = \sqrt{1 + u^2}, \quad b = (1 - u) \tan(\theta), \quad c = (1 + u) \tan(\theta) \). The function is plotted in figures 4(a) and (b). The wavelength with maximum intensity is varied depending on the twist angle. Considering the reflected mode of cell, this effect might be further intensified. The polarized ellipse was also dependent on the thickness of the LC cell (figure S20). As a result, the twist angle altered the wavelength with high intensity, and the LC domain exhibited different colors.

Additionally, the interference effect should be considered to explain the color change. A combination of constructive and destructive interference at different
wavelengths causes different colors. Since the optical anisotropy of nematic LC causes birefringence and the effective refractive index is given as [31]:

\[ n_{\text{eff}} = \sqrt{n_o^2 \sin^2 \theta + n_e^2 \cos^2 \theta} \]  

(6)

Considering the ordinary refractive index, \( n_o \), and extraordinary refraction index, \( n_e \), for 5CB, the \( n_{\text{eff}} \) was calculated (figure 4(c)). It was evident that \( n_{\text{eff}} \) was linearly dependent on twist angle. Constructive (\( 2n_{\text{eff}}d = m\lambda \)) or destructive (\( 2n_{\text{eff}}d = (m + 1/2)\lambda \)) interference is expected depending on \( n_{\text{eff}} \). Figure 4(d) shows the change of wavelength depending on different refractive indices, satisfying equation (6), where \( d = 1 \mu m \) and \( m = 4, 5, 6 \). Twisting by a field changes \( n_{\text{eff}} \), which changes the wavelength of constructive or destructive interference, and different color was displayed. This interference effect influences the color change, which is complementary to the modified Gooch–Tarry model. Moreover, when the polarized beam is reflected from the substrate, the color spectrum may be slightly changed due to the additional interference effect at the SiO\(_2\) layer on the silicon substrate.

The color display using aforementioned effects has some limitations, such as low color purity, narrow color spectrum, and limited viewing-angle. In order to be applied for a full color display, the LC director needs to be twisted further with multi-pitch. This color implementation with helical LC structure has been adopted in cholesteric liquid crystal displays [19, 28, 32, 33]. The wavelength of the reflection band is given by \( \lambda = p(n_e + n_o)/2 \), where \( p \) is the pitch length of the helical arrangement of the LC layer [28]. For that purpose, a chiral dopant can be added or the nematic LC should be replaced with a cholesteric LC. Then, the LC can be twisted continuously, with repeated pulse sequences in rotating direction to adjust the pitch. With this reflection band control, a full color display can be implemented.

**Voltage-dependent tuning**

To estimate the threshold voltage \( V_{\text{th}} \), pulses with different voltages up to \( \pm 1 \, \text{V} \) were applied transiently and POM images were taken as shown in figure 5. In figure 5(a), an electric field from left to right was applied between two parallel electrodes, and grains 1 and 3 were converted to green at around \( \Delta V = 12 \, \text{V} \),

![Figure 4](image-url)

*Figure 4. Theoretical estimation of transmittance as function of twist angle: (a) and (b) relation between transmittance and twisted angles was plotted for various wavelengths (\( \lambda = 450, 530, \) and \( 600 \, \text{nm} \)), for the cells with widths (a) 2 \( \mu m \) and (b) 3 \( \mu m \), respectively. The wavelength with strong intensity is varied depending on the twist angle. (c) The effective index of twisted LC due to birefringence was plotted as a function of twist angle. (d) The wavelengths causing constructive and destructive interferences of reflected beam from LC cell were plotted as functions of the effective index.*
which is approximately corresponding to the threshold voltage for LC domain reorientation. At this voltage, the electric force from the external field becomes equal to the anchoring force holding the LC to the initial orientation ($\phi_i = 0$), and the directors start jumping to the next preferential orientation ($\phi_f = 60^\circ$). Considering the distance between electrodes ~10 $\mu$m, the threshold electric field intensity $E_{th} = 1.2$ V $\mu$m$^{-1}$ was estimated, which is much lower than that of bistable LC on four-fold symmetry patterned polyimide reported by Kim et al [34]. This measurement was repeated to determine the threshold voltage on another sample with different shape of the grain, and similar threshold field was obtained (figures S21 and S22). Further increasing the field strength converted grain 4 to entirely green. The difference of the threshold voltage can be attributed to the defects of the grain. In order to explain this behavior, we suggest a model with a tilted crystal orientation of h-BN as shown in figure 5(c). Three armchair directions were indicated as ‘a’, ‘b’, and ‘c’. Assuming that initial orientation of LC was ‘a’, LC is rotated to ‘b’ clockwise by the field to $+x$ direction. When the field is applied to $-x$ direction, LC is rotated counterclockwise to ‘c’ at low field, but eventually moves to ‘b’ at high field. This demonstration confirms that all three states can be achieved by controlling the field strength and direction with two in-plane electrodes. On the other hand, no change on grain 2 can be explained by the fact that the LCs on the grain were initially oriented parallel to the external field.

The azimuthal anchoring strength of the liquid crystal/h-BN interface can be estimated from the threshold voltage. As the grain size of the h-BN is large, we can assume that the anchoring extrapolation length is smaller than the LC domain size [34]. The helical structure of the LC layers can be described by the azimuthal angle of the director, $\phi$, which is a function of the distance from the surface. The anchoring

Figure 5. Voltage dependent measurement: to measure the threshold voltage, the pulse voltage was varied from $-10$ to $10$ V. Four grains located in two parallel electrodes were numbered. (a) In case of field direction from left to right, grains 1 and 3 were converted to green around $\Delta V = 12$ V. By further increasing the field strength, grain 4 was converted to green. (b) When the field direction was changed, all three grains were converted to green at the same voltage. On further increase in the field strength, all three grains became orange. (c) To explain this behavior, a model with tilted crystal orientation of h-BN is suggested. The scale bars indicate 5 $\mu$m in all panels.
energy is mainly determined by the azimuthal angle difference $\Delta \varphi$ at the interface. The anchoring energy is expressed by the Rapini-Papoular function [35, 36] $W(\Delta \varphi) = \left( W_0 / 2 \right) \sin^2 (\Delta \varphi)$ in general, where $W_0$ is the anchoring strength. In this hexagonal symmetric substrate, the anchoring energy will have a maximum value at $\Delta \varphi = \pi/6$. As the electric force reaches the threshold point, the LC director jumps to a next preferential orientation, resulting in color switching.

The threshold field for bistable LC molecules on a fourfold symmetrical surface was calculated by Kim et al using the minimization of free energy with Rapini-Papoular anchoring energy [34] as

$$E_{th} = W_0 / \left( 2 \sqrt{K_{22} \Delta \varepsilon} \right), \quad \text{ (7)}$$

Where $K_{22}$ is the twist constant $(2 \times 10^{-12} \text{ N})$ and $\Delta \varepsilon$ is the dielectric anisotropy $(7 \times 10^{-11} \text{ F m}^{-1})$ [37]. Resultant anchoring strength, $W_0$, was estimated to be $\sim 10^{-8} \text{ J m}^{-2}$. The anchoring strength with the hexagonal symmetry ($\Delta \varphi = \pi/6$) is approximately estimated as $W_0 \approx 2.8 \times 10^{-5} \text{ J m}^{-2}$ from equation (7) and the measured threshold electric field $E_{th} = 1.2 \text{ V \mu m}^{-1}$, which is stronger than that of the rubbed PMMA layer, but weaker than that of a nanoscale patterned polyimide layer [38]. This result shows that the anchoring strength was enough to be utilized for display applications. It is notable that this anchoring force is not only based on the topographical structure of the surface, but also based on the crystallographic structure of the hexagonal lattice.

Using DFT calculations, we checked an external field effect on the orientation of a 5CB molecule on an h-BN nanoribbon (width $\sim 2\text{nm}$) in the zigzag and the armchair direction (figure S10). The two optimized structures were obtained in the absence of external electric field, and then a uniform external electric field was applied to the structure. The electric dipole moment of a 5CB molecule was estimated to be 6.61 D from DFT calculation, and a torque is experienced under the electric field. However, the permanent dipoles are cancelled out in a collective mode, and the induced dipole interaction should be considered. The LC molecules are rotated to be parallel to the electric field to minimize the free energy based on the dielectric anisotropy [39]. However, the opposite twist of LC depending on the field polarity cannot be explained by the dielectric anisotropy. Two possible scenarios can be considered to explain this behavior: (i) surface polarization or (ii) flexoelectric effect. In the first case (i) the adsorbed molecules on the h-BN are assumed to align unidirectionally, and non-zero spontaneous polarization is presumed at the interface. In the second case (ii) the flexoelectric effect is based on the density gradient near the interface. While the molecules anchored to the h-BN surface have its discrete possible adsorption sites, the molecules in bulk state do not have preferential sites. Thus, relatively low packing density near the interface is expected. Due to the shape anisotropy, more head groups tend to face the h-BN than tail groups, and non-zero polarization is induced at the interface. As described earlier, the adsorption energy of the 5CB molecule along the armchair direction is stronger than that in the zig–zag direction in the absence of applied electric field. In contrast, the orientation of the 5CB molecule prefers to the zig–zag direction, when the intensity of the electric field is larger than 0.03 V Å$^{-2}$. When placed in an external electric field, an object with an electric dipole moment tends to align parallel to the field to make potential energy lower. As this simulation is based on single LC molecule and nanosized substrate, the threshold electric field was estimated to be much stronger than the experimental result with collective LC dipole array.

**Conclusion**

In this work, an inventive method for realizing multistate of LC molecules on grains of h-BN has been proposed. The alignment of the LC was tuned via planar electric field. Several states with a variety of colors were confirmed by just varying the intensity of DC pulses. From electro-optical measurements, possibilities of novel display of various colors on a single pixel have been suggested. The new design paradigm presented in this work, provides an approach towards the realization of filter-free non-volatile displays without backlight unit. Owing to the molecular alignment symmetry of the LC on the hexagonal lattice, we insist that an ultra-high resolution display with a molecular-scale pixel can be realized.

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**Supporting information**

Supporting information [40, 41] with supplementary data set is available for this article.

Supporting video shows a real-time POM image of LC device with three electrode.

**Appendix**

From

$$\psi = \frac{a - ic}{a + ib} e^{i \theta}.$$  

Considering $r = \sqrt{a^2 + b^2}$, $r' = \sqrt{a'^2 + b'^2}$, $g = \tan^{-1} \frac{b}{a}$ and $g' = \tan^{-1} \frac{b'}{a'}$, we obtain.
\[ \psi = \frac{r'}{r} e^{i(g' - g + 2\theta)}. \]

As the analyzer was set in \( y \)-axis, imaginary part of \( \psi \) should be proportional to the detected intensity.

\[ \text{Im}(\psi) = \frac{r'}{r} \sin(g' - g + 2\theta). \]

Or,

\[ \text{Im}(\psi) = \frac{\sqrt{a^2 + c^2}}{\sqrt{a^2 + b^2}} \sin(\tan^{-1} \frac{c}{a} - \tan^{-1} \frac{b}{a} + 2\theta). \]

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