

In-Plane Switching Mode for Liquid Crystal Displays Using a DNA Alignment Layer

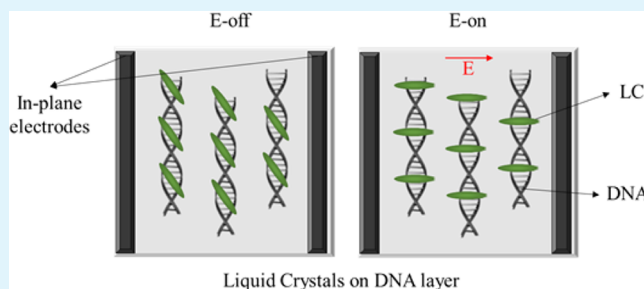
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ABSTRACT: We successfully fabricated the in-plane switching mode (IPS) LC display (LCD) based on a double stranded DNA (dsDNA) alignment layer. As widely known, the DNA has the right-handed double helical structure that has naturally grown grooves with a very regular period, which can be used as an alignment layer to control the orientation of liquid crystal (LC) molecules. The LC molecules on this topographical layer of DNA material align obliquely at a specific angle with respect to the direction of DNA chains, providing an instant and convenient tool for the fabrication of the IPS display compared to the conventional ways such as rubbing and mechanical shearing methods. The electro-optical performance and response time of this device were also investigated. Our result will be of great use in further exploration of the electro-optical properties of the other biomaterials.

KEYWORDS: DNA, biomaterial, liquid crystal, alignment layer, IPS LCD



1. INTRODUCTION

Deoxyribonucleic acid (DNA) is one of the most abundant biological molecules in nature. There are numerous simple, inexpensive, and rapid protocols for extracting crude DNA^{1,2} from plants and animals, which enables DNA material to be a kind of building block for practical applications.^{3–5} For example, well-purified λ -DNA (contour length $l_c \approx 16.3 \mu\text{m}$, 48 502 bp, persistence length $l_p \approx 50 \text{ nm}$), purchased from New England BioLabs, Inc., costs approximately \$250/mg, while crude DNA material ($l_c \approx 75\text{--}4000 \text{ nm}$, 200–12 000 bp, $l_p \approx 50 \text{ nm}$) purchased from Sigma-Aldrich costs approximately \$0.20/mg. Although variations in length along the DNA chain axis and nucleotide sequences exist in crude DNA materials, the chiral properties including handedness and periodicity of nucleotides and phosphates are the same with well-prepared expensive DNA materials. Since these regular topographical characteristics exist, DNA can be used as an alignment layer to guide other materials, such as particles, biopolymers, liquid crystals (LCs), etc., at the nanometer scale.^{6–12} Among these, an LC is one of the best candidates for functional materials to be guided, because LCs could easily respond to the interfacial force due to their anisotropic structure and fluidity.¹³ To use DNA as an alignment layer in this strategy, the orientation and ordering of DNA molecules have to be controlled on a large area of certain substrates, which can be achieved with molecular combing,¹⁴ magnetic fields,¹⁵ shear,⁸ and topographic confinement.^{16,17} However, such conventional methods present obstacles that must be surpassed to achieve well-controlled DNA films for the alignment layer applications.

Few studies have explored the interaction of LC molecules with underlying DNA molecules, in which LC molecules are

not aligned along with the long axis of shear-aligned DNA; instead, LC molecules are guided through the helical phosphate grooves of DNA with a specific angle of around 35° .^{8,18} This unusual orientation results from the topographical characteristics of the DNA-LC molecule, as well as charge density. Preliminary experimental responses of LC molecules on DNA have been shown previously,^{8,18} but they are inadequate to leverage DNA as an alignment layer for useful application, such as LC displays.

In the conventional manufacturing process of LCDs, rubbed polyimide (PI) films are predominantly used as alignment layers to control the ordering and orientation of LC molecules. However, the mechanical rubbing method is a slow process. The PI materials based on the rubbing method need an additional annealing process at a high temperature ($\sim 200^\circ\text{C}$) and extended period ($\sim 2 \text{ h}$), which can deteriorate the electro-optical properties of the LCD.¹⁹ In contrast, the inclined orientation of LC molecules in an LCD cell can easily and spontaneously be obtained using a DNA alignment layer that has intrinsic oblique grooves at room temperature.

In this work, we fabricated an in-plane switching mode (IPS) LC display using crude DNA material (Figure 1). The IPS mode, which has been most widely used, was adopted for our experiment because this mode has many advantages such as wide-viewing angle, clear images, and stable response time.^{20,21} To get the highly aligned, large area DNA film for this purpose, a simple brushing method was used. The DNA molecules were

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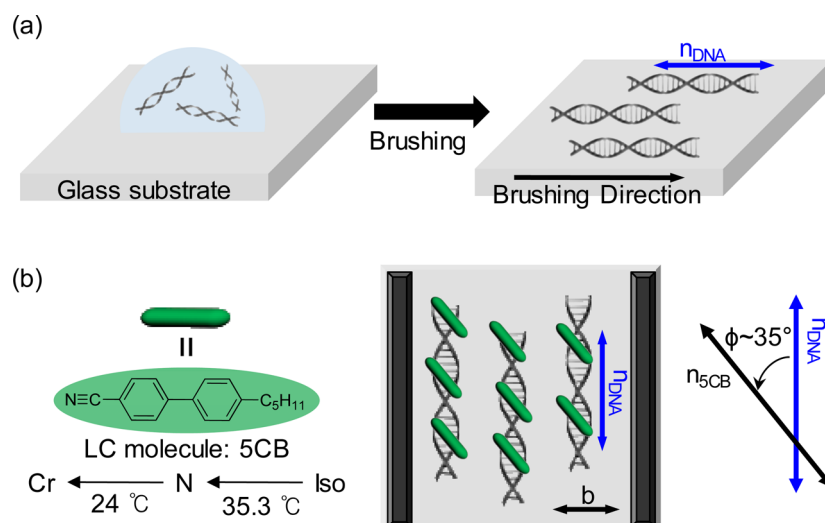


Figure 1. Preparation of the DNA alignment layer and oriented LC molecules. (a) Schematic illustration of the unidirectional DNA film that was aligned parallel to the brushing direction on the substrate. (b) Molecular structure of the LC and schematic sketches of aligned LC molecules on the DNA alignment layer. The ITO substrate for this experiment has patterned in-plane electrodes, and the DNA chains are aligned parallel to the electrodes.

combed parallel to the brushing direction by the shear stress during brushing of the DNA film, and optical properties of aligned DNA film were measured using depolarized transmission light microscopy (DTLM) and a spectrometer. Then, the IPS LCD was fabricated, and the electro-optical performances and response time of this device were investigated. Our result lays the foundations for further exploration of the electro-optical properties of biomaterials and offers a novel innovation for many related applications.

2. RESULTS AND DISCUSSION

For the IPS LCD based on DNA alignment layer, two substrates were initially prepared: one is a normal glass slide, and the other is a patterned indium tin oxide (ITO) substrate that has electrodes with in-plane electric field geometry where stripe electrodes were $10 \mu\text{m}$ in width and $10 \mu\text{m}$ in space (Figure 2a). On both substrates, the crude dsDNA that was purchased from Chitose Institute of Science and Technology was dissolved in deionized water at $\sim 20 \text{ wt } \%$, spread, and sheared along with the electrodes with a normal makeup brush (Olive Young Shadow Brush #6, KC Korea) to get an aligned DNA film with a director, n_{DNA} (Figure 1a). Then, the cell was made by sandwiching these substrates parallel to each other and spaced by $3 \mu\text{m}$ with spherical silica particles after drying the aligned DNA film. Additionally, the LC molecule, 4-cyano-4'-pentylbiphenyl (5CB), was injected by capillary force at the isotropic phase (40°C), which aligned along with helical groove of DNA at $\sim 35^\circ$ (Figure 1b).

The optical properties of the aligned DNA film were probed by (i) DTLM (LV100POL, Nikon) to examine the optical textures and orientation distribution of n_{DNA} , and by (ii) a spectrometer (USB-2000+, Ocean Optics) to investigate the orientation of the DNA alignment layer as a function of rotation angle. Despite the simple preparation method of brushing by hand, these techniques provided unambiguous evidence of the alignment of the DNA on the substrate. The transmitted light intensity mainly varies as $I \propto \sin^2 2\theta$, depending on the angle between a principal optic axis (n_{DNA}) and the polarization direction (P), θ (Figure 2b). The $\sin^2 2\theta$ term in I gives minimum transmittance for $\theta = 90^\circ + 90^\circ \times n$ (n is integer), and maximum intensity for $\theta = 45^\circ + 90^\circ \times n$.

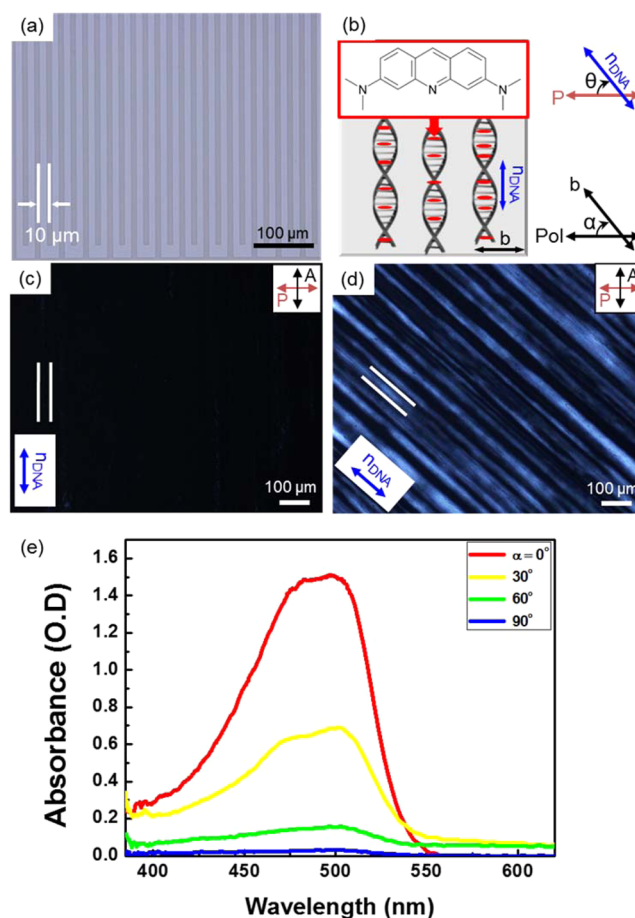


Figure 2. DNA alignment layer on the ITO substrate and fluorescent intensity of the DNA alignment layer. (a) Normal light microscopy image (transmission mode) of patterned in-plane electrodes. The pattern width and separation is $10 \mu\text{m}$. (b) A schematic sketch of aligned DNA chains and Acridine Orange dyes placed in the nucleotides. (c) DTLM images of the aligned DNA layer where the brushing direction is parallel to the analyzer (d) and at -45° to the analyzer. (e) Fluorescent intensity of the DNA alignment layer mixed with Acridine Orange dyes during the changing of the angles between b and Pol.

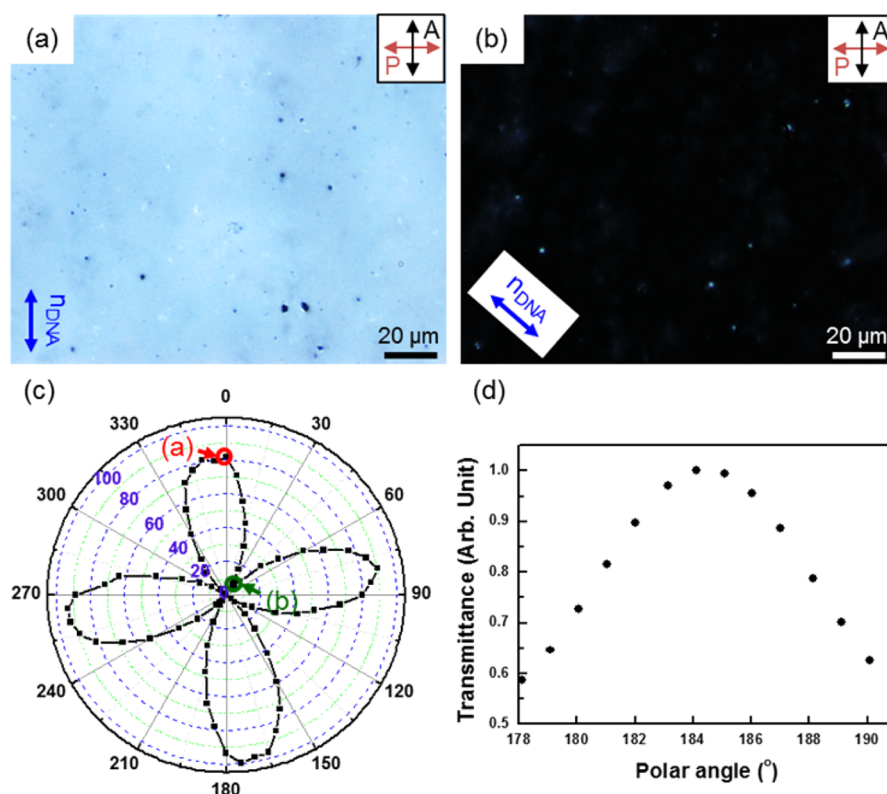


Figure 3. DTLM images of LC molecules on the DNA alignment layer, when the brushing direction is parallel (a) and at -35° (b) to the analyzer. (c) The polar plot shows the transmittance change of the sample as a function of the rotation angle between brushing direction and analyzer. The change of transmittance exhibited the periodicity of 90° , corresponding the intensity of the transmittance. (d) The transmittance tendency as a function of rotation angle of the LC cell based on the brushed DNA layer along with polar direction under crossed polarizers.

On the basis of these simple polarization characteristics, we can determine two kinds of orientations of DNA films: the birefringence is dark (Figure 2c) or bright (Figure 2d) when n_{DNA} is parallel or tilted to P , respectively.

To further probe the orientation of the DNA alignment layer, spectroscopic experiments were carried out. For this experiment, the specimen must be fluorescent. However, our DNA alignment layer did not exhibit autofluorescence. Thus, this sample was mixed with Acridine Orange (Figure 2b), a fluorescent probe to generate fluorescent signals depending on the alignment of DNA chains.^{16,22} As shown in Figure 2b, Acridine Orange molecules bind strongly to DNA nucleotides by intercalation between successive base pairs, showing an excitation maximum at 460 nm and exhibiting fluorescence with a maximum wavelength of 537 nm. The absorption and emission dipoles of Acridine Orange dye are parallel to its molecular long axis, which is normal to the long axis of the DNA chains (n_{DNA} in the intercalated state). Thus, the resulting absorption intensity is the highest when the excitation light is polarized normal to n_{DNA} ($\alpha = 0^\circ$) (Figure 2e). As observed above, the absorptive fluorescence intensity varies by $I \propto \cos^4 \alpha$, where α is the angle between the base pair direction b (Figures 1b and 2b) and polarization direction (Pol) of excitation light source. This offers a sensitive probe of DNA orientation and ordering. The absorbance was measured as a function of the angle α between the exciting Pol and base pair direction b (Figure 2e). In all cases, the strongest absorbance was observed when the excitation Pol is perpendicular to n_{DNA} ($\alpha = 0^\circ$), showing less absorbance as α is increased to 90° . The dependence on α indicates that the preferred orientation of the brushed DNA film (n_{DNA}) is parallel to the brushing direction

(Figure 1). Using the dichroic absorbance, we measured the order parameter of the DNA alignment layer along the brush direction. The order parameter S was calculated by using the following equation:²³ $S = (N - 1)/(N + 2)$, $N = \text{OD}_{\text{parallel}}/\text{OD}_{\text{perpendicular}}$, where $\text{OD}_{\text{parallel}}$ and $\text{OD}_{\text{perpendicular}}$ are the optical densities of the brushed DNA under the incident light to fluorescent dye with parallel and perpendicular direction, respectively. According to the absorbance data, $N = \text{OD}_{\text{parallel}}/\text{OD}_{\text{perpendicular}} = 1.51/0.03 = 50$. The order parameter S was calculated to be 0.94, indicating that our simple method can fabricate the highly aligned DNA film.

To verify the effect of brushed DNA layer on LC molecules, 5CB molecules were spin coated on the DNA brushed substrate at its isotropic temperature. When the n_{DNA} is parallel to the analyzer or polarizer, the cell exhibited a high light transmission (Figure 3a), while a good extinction was observed due to the inclined orientation of LC molecules when the n_{DNA} was rotated diagonally to the analyzer or polarizer. To confirm the angle between the LC director (n_{5CB}) and the brushing direction (n_{DNA}), the transmittance of LCs on the DNA alignment layer as a function of rotation angle between n_{DNA} and analyzer was recorded using a spectrometer with a light source at 550.14 nm (SPECTRA X, Lumencor).

The polar plot in Figure 3c shows 4-fold symmetry tilted from the cross-polarizers as expected from DTLM images. The lowest transmittance was measured at $\theta = 35^\circ + 90^\circ \times n$, while the highest transmittance was detected at $\theta = 80^\circ + 90^\circ \times n$ as expected in DTLM images (Figure 3c). This is due to the strongly anchored 5CB molecules in the polar grooves made of phosphate groups in the DNA chains, which has a characteristic oblique angle of $\phi \sim 35^\circ$ with respect to n_{DNA} (Figure 1b).⁸

This confirms that the LCs have an orientation order in a specific direction due to the DNA alignment layer, indicating that the brushed DNA film exhibits an excellent capability to align the nematic LC molecules. As an LC alignment layer of DNA film, the following characteristics are important: LC molecule alignment along the polar direction as well as the azimuthal direction from alignment layer. The polar angle (pretilt angle) of the LC molecules from the alignment layer under the absent electric field influences electro-optical performance including driving voltage, response time, and viewing angle.²⁴ In IPS LCD mode, the smaller pretilt angle is required for wide-viewing angle. To evaluate the DNA layer as LC alignment layer, we measured the pretilt angle of antiparallel LC cell based on the brushed DNA layer by rotating the cell to polar direction under crossed polarizers (Figure 3d). The pretilt angle of LC molecules from the brushed DNA film was about 4° , which is comparable to that of the conventional PI based LC cell ($2\text{--}3^\circ$).²⁵

Regarding the polar plot, the IPS LCD based on the DNA alignment layer can be illustrated as shown in Figure 4a. This is

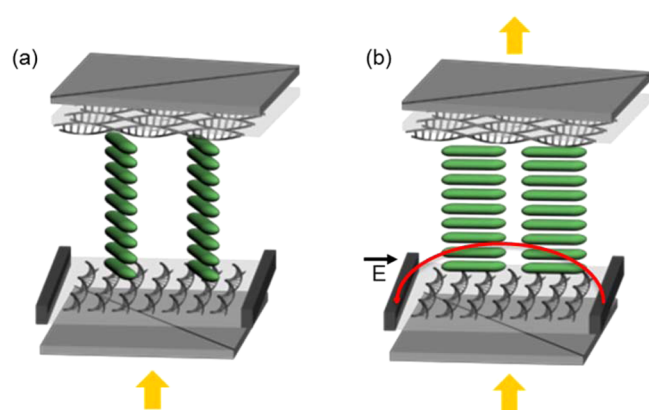


Figure 4. Illustration of the IPS LC cell based on the DNA layer. (a) Without the applied electric field, LC molecules aligned obliquely with the electrode direction, and thus, the polarized light getting through the LCs is blocked by the top-polarizer, resulting in a dark mode. (b) With the applied electric field, LC molecules reorient along the in-plane electrodes, and thus, the polarized light can be guided by the LCs to pass through the top-polarizer, giving a bright mode.

a dark mode, and thus, the polarized light of the bottom polarizer is blocked out by the top polarizer without applying an electric field (Figure 4a). Once the in-plane electric field (E) is applied to this cell, most 5CB molecules are aligned parallel to the E and the polarized light can be guided by the reoriented 5CB LC molecules to pass through the cell, resulting in a bright mode as illustrated in Figure 4b.

The electro-optical response of the IPS LCD was measured as a function of applying an ac electric field with 1 kHz. As mentioned above, the DTLM image of the cell without an electric field is very dark. The optical axis of the bottom polarizer was oriented parallel to the LC director (Figure 5a). The stripe patterns in the images are ITO electrode lines. The driving voltage of the cell (V_{th}) was $\sim 28 V_{rms}$, which corresponds to $E = 2.8 V/\mu m$. As the voltage exceeds V_{th} , the transmittance increases gradually because the LC director, n_{5CB} , reorients to follow the external electric field. Figure 5e is the voltage-dependent transmittance (VT) of the IPS LCD based on the DNA alignment layer. When the applied voltage was varied, the transmittance of the device changed, which is

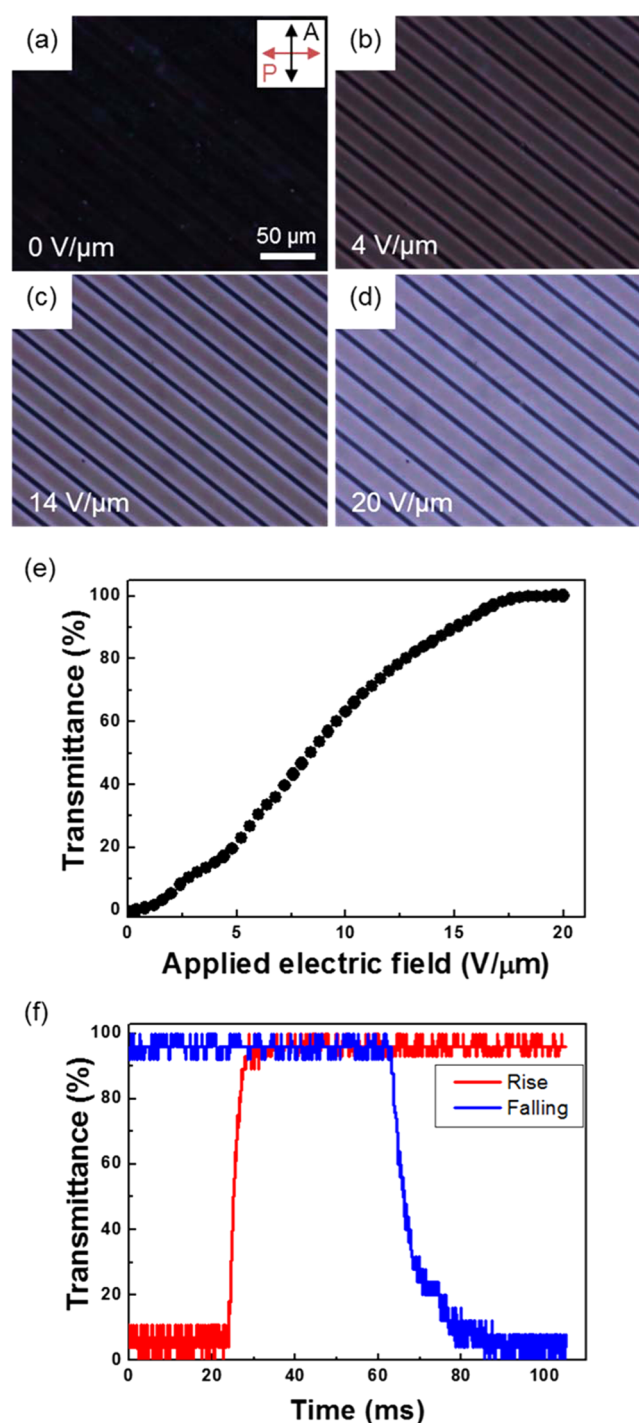


Figure 5. DTLM images of an IPS cell based on the DNA alignment layer: (a) With no field applied, the nematic phase of LCs are parallel to the polarizer direction, giving the extinction of the transmitted light. (b–d) With voltage applied, the reoriented LC molecules normal to the electrodes give the significant light transmittance between crossed polarizers. (e) A voltage-dependent transmittance curve and (f) response time of the cell.

important for gray scales for LCDs. The driving voltage of our sample is a little bit higher than that of PI-based IPS cell, which resulted from the manually coated DNA film that has relatively not-uniform thickness. We also observed the dynamic response of the LC molecules on DNA film during electrical switching (Figure 5f). The dynamic response indicates how a high quality

dynamic image of LCD can be performed. The rising time represents the time when LC molecules completely respond to applied field, while the decay time is the time LC molecules come back to the initial state right after turning off the electric field. The rising and decay times of our cell were 3.8 and 12.3 ms, respectively. The response time is comparable to conventional IPS LCD based on polyimide alignment layer.²⁶

3. CONCLUSION

In summary, we successfully fabricated an IPS display device based on the DNA alignment layer. The LC molecules on the naturally grown grooves of a regular period of DNA align obliquely at a specific angle with respect to the direction of DNA chains. This provides an instant and convenient tool for the fabrication of the IPS LCD compared to conventional methods, such as rubbing and mechanical shearing methods. The electro-optical performance and response time of this device were also investigated. Our results pave the way for further exploration of the electro-optical properties of biomaterials and offer an easy method for many other applications in optoelectronics in the future.

4. EXPERIMENTAL METHODS

Sample Preparation. To fabricate an IPS device based on a DNA alignment layer, we used dsDNA (received from Chitose Institute of Science and Technology) dissolved in deionized water with ~20 wt %. The DNA solution was brushed over two substrates where one is a cleaned typical glass slide, and the other is a patterned ITO glass with an in-plane electric field geometry (stripe electrodes of 10- μ m width and 10- μ m space) (Figure 2a). These two substrates were assembled to make a sandwich cell, in which the cell gap was maintained at 3 μ m by silica ball spacers. After the cell was made, 4-cyano-4'-pentylbiphenyl (5CB, Sigma-Aldrich) nematic liquid crystal (NLC) was injected by capillary force at the isotropic temperature (~40 °C).

Characterization. The optical textures were characterized by depolarized transmitted light microscopy (DTLM). The transmittance of LCs on the DNA alignment layer as a function of rotation angle between the brushing direction and analyzer was recorded using a USB-2000+ spectrometer (Ocean Optics) with a solid-state light source (SPECTRA X, Lumencor). The electro-optic (EO) performance was measured using a home-built equipment consisting of a halogen lamp, a function generator (33210A, Agilent), a voltage amplifier (A400, FLC Electronics), a silicon photodetector (S-025-H, Electro-Optical Systems), and a lock-in amplifier (SR830, Stanford Research Systems). The AC electric field (rectangular pulses of frequency $f = 1$ kHz) was applied to the cell.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Livolant, F.; Leforestier, A. Condensed Phases of DNA: Structures and Phase Transitions. *Prog. Polym. Sci.* **1996**, *21*, 1115–1164.

(2) Taggart, J. B.; Hynes, R. A.; Prodohl, P. A.; Ferguson, A. A Simplified Protocol for Routine Rotational DNA Isolation from Salmonid Fishes. *J. Fish Biol.* **1992**, *40*, 963–965.

(3) Steckl, A. J. DNA—A New Material for Photonics? *Nat. Photonics* **2007**, *1*, 3–5.

(4) Grote, J. Biopolymer Materials Show Promise for Electronics and Photonics Applications. *SPIE Newsroom* **2008**, 1082 <http://dx.doi.org/10.1117/2.1200805>.

(5) Kim, S. J.; Jung, J.; Lee, K. W.; Yoon, D. H.; Jung, T. S.; Dugasani, S. R.; Park, S. H.; Kim, H. J. Low-Cost Label-Free Electrical Detection of Artificial DNA Nanostructures Using Solution-Processed Oxide Thin-Film Transistors. *ACS Appl. Mater. Interfaces* **2013**, *5*, 10715–10720.

(6) Tanaka, K.; Okahata, Y. A DNA-Lipid Complex in Organic Media and Formation of an Aligned Cast Film. *J. Am. Chem. Soc.* **1996**, *118*, 10679–10683.

(7) Nakao, H.; Shiigi, H.; Yamamoto, Y.; Tokonami, S.; Nagaoka, T.; Sugiyama, S.; Ohtani, T. Highly Ordered Assemblies of Au Nanoparticles Organized on DNA. *Nano Lett.* **2003**, *3*, 1391–1394.

(8) Nakata, M.; Zanchetta, G.; Buscaglia, M.; Bellini, T.; Clark, N. A. Liquid Crystal Alignment on a Chiral Surface: Interfacial Interaction with Sheared DNA Films. *Langmuir* **2008**, *24*, 10390–10394.

(9) Becerril, H. A.; Woolley, A. T. DNA-Templated Nanofabrication. *Chem. Soc. Rev.* **2009**, *38*, 329–337.

(10) Katarzyna, M.; Joanna, O.-B. DNA as Scaffolding for Nanophotonic Structures. *J. Nanophotonics* **2012**, *6*, 064505–1–15.

(11) Lagerwall, J. P. F.; Scalia, G. A New Era for Liquid Crystal Research: Applications of Liquid Crystals in Soft Matter Nano-, Bio- and Microtechnology. *Curr. Appl. Phys.* **2012**, *12*, 1387–1412.

(12) Lowe, A. M.; Abbott, N. L. Liquid Crystalline Materials for Biological Applications. *Chem. Mater.* **2012**, *24*, 746–758.

(13) Ohzono, T.; Yamamoto, T.; Fukuda, J.-I. A Liquid Crystalline Chirality Balance for Vapours. *Nat. Commun.* **2014**, *5*, 1–7.

(14) Bensimon, A.; Simon, A.; Chiffaudel, A.; Croquette, V.; Heslot, F.; Bensimon, D. Alignment and Sensitive Detection of DNA by a Moving Interface. *Science* **1994**, *265*, 2096–2098.

(15) Kung, H. C.; Wang, K. Y.; Goljer, I.; Bolton, P. H. Magnetic Alignment of Duplex and Quadruplex DNAs. *J. Magn. Reson., Ser. B* **1995**, *109*, 323–325.

(16) Yoon, D. K.; Smith, G. P.; Tsai, E.; Moranc, M.; Wallbac, D. M.; Bellinid, T.; Smalyukha, I. I.; Clark, N. A. Alignment of the Columnar Liquid Crystal Phase of Nano-DNA by Confinement in Channels. *Liq. Cryst.* **2012**, *39*, 571–577.

(17) Xu, H.; Minter, C. J.; Nagasaka, S.; Ito, T.; Higgins, D. A. Elongation, Alignment, and Guided Electrophoretic Migration of ds-DNA in Flow-Aligned Hexagonal F127 Gels. *J. Phys. Chem. B* **2014**, *118*, 4151–4159.

(18) Malone, S. M.; Schwartz, D. K. Macroscopic Liquid Crystal Response to Isolated DNA Helices. *Langmuir* **2011**, *27*, 11767–11772.

(19) Lee, Y.-J.; Baek, J.-H.; Kim, Y.; Heo, J. U.; Yu, C.-J.; Kim, J.-H. Enhanced Surface Anchoring Energy for the Photo-Alignment Layer with Reactive Mesogens for Fast Response Time of Liquid Crystal Displays. *J. Phys. D: Appl. Phys.* **2013**, *46*, 1–5.

(20) Oh-e, M.; Kondo, K. Electro-Optical Characteristics and Switching Behavior of the In-Plane Switching Mode. *Appl. Phys. Lett.* **1995**, *67*, 3895–3897.

(21) Oh-e, M.; Kondo, K. Response Mechanism of Nematic Liquid Crystals Using the In-Plane Switching Mode. *Appl. Phys. Lett.* **1996**, *69*, 623–625.

(22) Smalyukh, I. I.; Zribi, O. V.; Butler, J. C.; Lavrentovich, O. D.; Wong, G. C. L. Structure and Dynamics of Liquid Crystalline Pattern Formation in Drying Droplets of DNA. *Phys. Rev. Lett.* **2006**, *96*, 177801–1–4.

(23) Wang, Y.-J.; Carlisle, G. O. Optical Properties of Disperse-Red-1-Doped Nematic Liquid Crystal. *J. Mater. Sci.* **2002**, *13*, 173–178.

(24) Masahito, Oh-E.; Makoto, Y.; Masuyuki, O.; Katsumi, K. Dependence of Viewing Angle Characteristics on Pretilt Angle in the In-Plane Switching mode. *Liq. Cryst.* **1997**, *22*, 391–400.

(25) Hwang, S.-J.; Yu, H. H.; Hsu, M.-H. Determining the Liquid-Crystal Polar Anchoring at High Electric Fields by Heterodyne Interferometer. *J. Disp. Technol.* **2007**, *3*, 259–265.

(26) *Handbook of Visual Display Technology*; Chen, J., Cranton, W., Fihn, M., Eds.; Springer Verlag: Berlin, 2011.