Surface-Mediated Photoalignment of Discotic Liquid Crystals on Azobenzene Polymer Films

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This paper describes a simple strategy for the formation of photoaligned and micropatterned discotic liquid crystal (DLC) film on the surface of photoirradiated azobenzene-containing polymer thin film. The key material for the surface-mediated photoalignment of the DLCs was poly[4-(4-cyanophenylazo)phenyl methacrylate] (pMAzCN). Optical anisotropy was generated in a pMAzCN film by oblique exposure to nonpolarized light which resulted in angle-selective photoisomerization and reorientation of the azobenzenes. Subsequent annealing of the film at 240 °C enhanced the photoaligned state of the *p*-cyanoazobenzenes due to strong intermolecular dipole−dipole interaction and semicrystalline nature of the pMAzCN. This combination of photoirradiation and subsequent annealing of the pMAzCN film made it possible to realize the surface-assisted orientation control of a DLC molecule, which displays both columnar (Col) and discotic nematic (N$_D$) phases over 152 °C. When the pMAzCN film was exposed to linearly polarized light from the surface normal, the DLC molecules showed homeotropic orientation with the director perpendicular to the substrate surface. In the contrast, oblique irradiation of the pMAzCN film with nonpolarized light gave rise to tilted DLC orientation with well-ordered optical birefringence at the N$_D$ phase. Rapid cooling from the N$_D$ phase produced a well-aligned glassy N$_D$ state at room temperature, which was adequately stable for 10 months even though no covalent cross-linking among the DLCs was performed. The spatial orientation of photoaligned DLCs in both their bulk film and in their interface region was characterized by means of optical birefringence, X-ray diffraction, and fluorescence measurements. At the N$_D$ phase, the DLC molecules were aligned in a hybrid manner such that their tilt angles varied throughout the thickness of DLC film. The direction of tilted DLCs was opposite to the propagation of the actinic nonpolarized light. The photoaligned DLC films exhibited polarized fluorescence emission with an *s*-polarized/*p*-polarized intensity ratio of 4.1, despite the nonpolarized excitation of only DLC at outmost surface. These results indicate that the three-dimensionally aligned azobenzene moieties of the pMAzCN thin film were transferred to the tilted DLC molecules at air/DLC interface. Finally, we demonstrated micrometer-scale photopatterned orientation of DLC molecules on the pMAzCN surface by oblique nonpolarized irradiation of the film through a photomask.

1. Introduction

The discovery of disk-shaped liquid crystals, that is, discotic liquid crystal (DLCs), by Chandrasekhar[1] has led to novel findings in research on other kinds of the chemical structures,[2] as well as on the unique physical properties of DLCs, including their electrical conductivity,[3] photoconductivity,[4] photovoltaic properties,[5] photoluminescence,[6] electroluminescence,[7] and nonlinear optical properties.[8] The DLC materials have recently attracted a great deal of attention for their versatility and potential application to novel nanodevices for next-generation photonics and electronics. DLC molecules are mostly composed of a two-dimensionally π-conjugated central core, such as triphenylenes, coronenes, porphyrins, phthalocyanines, and so forth, surrounded peripherally by several flexible aliphatic chains, giving rise to thermally induced polymesomorphism, which is typically categorized into columnar (Col) and discotic nematic (N$_D$) phases.[2] The simplest discotic columnar phase has a long-range transitional periodicity in two-dimensional as a result of intermolecular stacking among the DLCs, leading to the formation of parallel columns of supramolecular assemblages with liquid-like disorder. On the other hand, the N$_D$ phase possesses only parallel orientation with respect to each DLC plane. Most DLC materials display the Col mesophase due to the strong self-organization of the π−π interaction between their rigid central cores, whereas few compounds show the N$_D$ phase. The current progress of research in the field of DLCs seems to be trailing behind that of the conventional calamitic liquid crystals (CLCs). This has probably been due to the difficulties encountered in assembling well-defined DLCs, arising from their

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intrinsic physical properties, such as high viscosity and high mesophase temperatures, which resulted from the strong intermolecular interaction among the DLCs. Accordingly, although there have been hitherto a few reports on well-defined, organized assemblages of the DLC molecules produced by the surface-mediated techniques using mechanically rubbed polymer films[9] and substrates deposited with inorganic compounds,[10] there has been little headway made in comprehending the orientational mechanism of DLCs on a substrate surface at the interfacial molecular level. However, there has recently been a trend in advanced nanotechnology toward investigation into the orientational control and patterning of disk-shaped molecules and their supramolecular aggregates, due to the necessity to optimize anisotropic properties in novel nanodevices.[11,12]

We have previously investigated the surface-mediated orientational photocontrol of conventional CLCs by utilizing photoreactive polymer thin films, self-assembled molecular films, and Langmuir−Blodgett monolayers containing azobenzenes, cinnamates, and so forth as photoreactive moieties.[13] When a thin film of photoreactive polymer, for instance, is exposed to linearly polarized light or obliquely nonpolarized light, optical anisotropy is generated as a result of the angle-selective photochemical reactions. This is critically determined by the interplay of the electric dipole transition moment of the photoreactive chromophore with the electric vector of the irradiating light. Consequently, the photoinduced molecular orientation of the films is transferred to the CLC molecules producing homeotropic, homogeneous, and even tilted CLC alignment within the bulk CLC layers. This results from the self-organizing tendency of the bulk CLC layers to amplify the negligible information, such as the molecular conformation and orientation, closest to its substrate surfaces. When this CLC photoalignment method is applied to the orientational photocontrol of DLCs molecules, some problems arise concerning the thermal stability of the photoaligned molecular ordering of the films. The mesophase temperature at which the molecular orientation of DLCs occurs is high—typically over 150 °C.[2] Previously, we reported preliminary success applying a simple and comprehensive strategy to control the DLC orientation through the photoalignment of thin films of a poly[4-(4-cyanophenylazo)phenyl methacrylate] (pMAzCN; Figure 1A).[14] However, at the molecular level, the mechanism behind the relationship between the orientational identification of the DLC molecules and the photoaligned azobenzene moieties of the pMAzCN films remains obscure. The present report details the spatial orientation of DLCs on photoirradiated pMAzCN films analyzed by means of optical birefringence, X-ray diffraction, and fluorescence measurements in order to establish a novel guideline for DLC photoalignment. Our photochemical procedure to align the DLC molecules using pMAzCN films offers potential advantages for the on-demand control of DLC orientation at the interfacial molecular level, which is of fundamental importance for the design and fabrication of novel nanodevices.

2. Experimental Section

2.1. Materials. The chemical structures of the materials used in this study are shown in Figure 1. A poly(methacrylate) possessing *p*-cyanoazobenzene side chains, i.e., pMAzCN (Figure 1A), was synthesized by our previously reported method.[15] The physical properties of pMAzCN were M_W of 4.3 $\times 10^4$ and M_W/M_N of 3.3. This polymer exhibited extraordinarily high temperature of T_g at 185 °C and no isotropic phase up to 250 °C. Figure 1B shows two kinds of triphenylene derivatives modified with alkoxylbenzoyl groups at six positions surround-
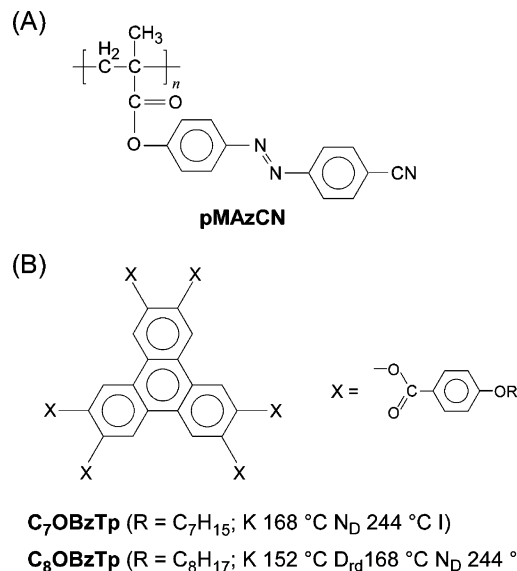

C$_7$OBzTp (R = C$_7$H$_{15}$; K 168 °C N$_D$ 244 °C I)

C$_8$OBzTp (R = C$_8$H$_{17}$; K 152 °C D$_{rd}$168 °C N$_D$ 244 °C I)

Figure 1. Chemical structures of the materials used in this study: (A) poly(methacrylate) bearing *p*-cyanoazobenzene in the side chain (pMAzCN); (B) two kinds of triphenylene discotic liquid crystals tethering the different alkyl side chain lengths of C$_7$ (C$_7$OBzTp) and C$_8$ (C$_8$OBzTp). C$_7$OBzTp shows only the discotic nematic (N$_D$) phase, whereas both the columnar (Col; discotic rectangular) and N$_D$ phase appear for C$_8$OBzTp.

ing of the DLC core material used in this study; C$_7$OBzTp and C$_8$OBzTp stand for 2,3,6,7,10,11-hexakis(4-heptyloxybenzoyloxy)triphenylene and 2,3,6,7,10,11-hexakis(4-octyloxybenzoyloxy)triphenylene, respectively. These compounds were synthesized by the reaction of 2,3,6,7,10,11-hexahydroxytriphenylene with alkoxybenzoyl chloride in the presence of 4-(dimethylamino)pyridine, as described previously.[16] The C$_8$OBzTp exhibited both columnar (Col) and discotic nematic (N$_D$) phases, whereas the mesophase of C$_7$OBzTp was only the N$_D$ phase. The Col mesophase structure corresponded to a two-dimensional rectangular lattice of columns in which the DLC molecules were stacked in a disordered manner. The N$_D$ phase was restricted to solely parallel orientation with respect to the DLC plane. The overall phase sequences were *K* 168 °C N$_D$ 244 °C *I* for C$_7$OBzTp and *K* 152 °C Col 168 °C N$_D$ 244 °C *I* for C$_8$OBzTp.[16]

2.2. Sample Preparation and Photoirradiation. A pMAzCN thin film with 20 nm thickness, obtained on a fused silica substrate by spin-coating with a 1.0 wt % solution of the polymer in cyclohexanone, was exposed to nonpolarized light from an oblique incident angle or linearly polarized light from the surface normal. Photoirradiation was performed using a 150 W Hg−Xe lamp (San-ei Electric MFG. Co., UV Supercure-230S) through both cutoff and band-pass filters (Toshiba, UV-35 and UVD-36A for 365 nm; Y-44 and V-42 for 436 nm), and the light intensity was measured by an optical power meter (Advantest, TQ8210). Subsequently, the photoirradiated polymer film was annealed at an appropriate temperature using a hot stage (Mettler, FP800) and coated with a 20 wt % solution of DLC in 4-methyl-2-pentanone to obtain a DLC film with ca. 1 µm thickness.

2.3. Physical Measurements. Electronic absorption spectra were acquired on a photodiode array spectrophotometer (Hewlett-Packard, 8452 A). Optical textures of the DLCs were observed by a polarized optical microscope (Olympus, BH-2) equipped with a high-gain color camera. Conoscopic images were obtained by attaching a Bertrand's lens and a wave retardation plate to the microscope. Optical phase retardation of the films

was measured by means of a polarization-modulating transmission ellipsometer (JASCO, BFA-150) equipped with a probing He−Ne laser beam at 633 nm and a photoelastic modulator (PEM) controlling polarization at a modulation frequency of 50 kHz. This optical system conveniently provided measurement of two ellipsometric parameters, i.e., optical phase difference angle (Δ) and relative amplitude ratio (Ψ), when the DLC film was rotated from $-60°$ to $+60°$ with respect to the surface normal. Δ indicates the difference in optical phase velocity between s- and p-polarization of the probing He−Ne laser beam with respect to the DLC film ($\Delta = \Delta_s - \Delta_p$). Fluorescence and fluorescence excitation spectra were recorded with a spectrofluorometer (JASCO, FP-777) under argon gas flow. X-ray diffraction (XRD) (Philips, X′Pert PW 1711) was performed using Cu K_a radiation at a wavelength of 1.54 Å in the 2θ range between $1°$ and $30°$.

3. Results and Discussion

3.1. Photoinduced Dichroism. When thin films of azobenzene-containing polymers are exposed to linearly polarized light[17] or to oblique nonpolarized light,[18] the excited azobenzenes undergo the reorientation toward the nonexcited direction. With irradiation by linearly polarized light, the azobenzene orientation becomes approximately perpendicular to the polarization axis of actinic light,[17] while in the case of oblique nonpolarized light, it is parallel with the actinic light propagation.[18] Although most of such films thus exposed show negligible values for both photodichroism and optical anisotropy, their photoinduced molecular orientation enables the formation of bulk nematic CLC layers with homogeneous and even tilted alignment.[18a] This is made possible by the molecular harmonization occurring in the bulk CLC layers which amplifies small anisotropy on the substrate surfaces. Before examining the photocontrolled orientation of DLCs on pMAzCN film, we evaluated the order of the film's photoinduced orientation through polarized absorption spectrum measurement before and after oblique nonpolarized or linearly polarized irradiation.

3.1.1. Obliquely Nonpolarized Exposure. First, the pMAzCN thin film was exposed obliquely to nonpolarized 436 nm light at a dose of 3.0 J cm^{-2} at an incident angle of 45° from the normal and then annealed at 240 °C for 30 min. Changes in the polarized absorption spectra are shown in the Supporting Information. The as-coated pMAzCN film exhibited no optical anisotropy having absorbances of 0.25 at around 330 nm. The oblique nonpolarized light exposure brought about a small decline in absorbance due to E-to-Z photoisomerization. The absorption spectrum of the pMAzCN film with the electric vector parallel with the incident plane of the actinic nonpolarized light was slightly larger than that with the electric vector perpendicular to the incident plane. The dichroic ratio (DR_{NPL}) induced by the nonpolarized exposure was to quantitatively evaluate the azimuthal orientational order of azobenzenes. The DR_{NPL} value is defined here as

$$DR_{NPL} = (A_1 - A_2)/A_0 \qquad (1)$$

where A_1 and A_2 correspond to the absorbances at the maximum absorption wavelength attributable to the $\pi-\pi^*$ transition of E-azobenzene, as monitored by probing polarized light with the electric vectors in parallel with and perpendicular to the incident plane of the nonpolarized light, respectively.[18a] A_0 indicates the absorbance of 0.25 before irradiation. After oblique exposure, a tiny dichroic ratio of $DR_{NPL} = 0.04$ was estimated. This was because the longitudinal axis of the E-isomer of the azobenzenes

TABLE 1: Changes in the Dichroic Ratio of pMAzCN Film after Photoirradiation and Subsequent Annealing at 240 °C

	after irradiation with 436 nm light of 3.0 J cm^{-2}	after subsequent annealing at 240 °C for 30 min
$DR_{NPL}{}^a$	0.04	0.16
$DR_{LPL}{}^b$	0.14	0.48

^{a} The dichroic ratio (DR_{NPL}) for oblique nonpolarized exposure is defined by eq 1. ^{b} The dichroic ratio (DR_{LPL}) for perpendicular exposure to linearly polarized light is defined by eq 2.

became inclined toward the incident plane of the actinic nonpolarized light minimizing light absorption. Interestingly, when the photoirradiated film was annealed at 240 °C, i.e., even above pMAzCN's T_g of 185 °C, the difference in the polarized spectra between parallel-with and perpendicular-to the incident plane was enhanced to a DR_{NPL} value of 0.16 from 0.04. These polarized spectrum measurements revealed a blue-shift in the maximum absorption wavelengths of the E-azobenzenes (see the Supporting Information). This thermal enhancement of the photoaligned states probably arose from not only the preferable H-aggregation of polar and rigid p-cyanoazobenzenes in the polymer matrix, but also the semicrystallinity of pMAzCN. This is consistent with previous observations reported for other films of liquid crystalline[19] and semicrystalline azobenzene-containing polymers[20] treated by exposure to linearly polarized light. In contrast, amorphous polymers display a complete disappearance of photodichroism upon heating above their T_g's.[21] In addition, we found that the absorption spectra of both A_1 and A_2 decreased remarkably after the annealing treatment of the obliquely nonpolarized light exposed pMAzCN film (see the Supporting Information), which probably indicates reorientation of the E-azobenzenes toward the surface normal.

3.1.2. Linearly Polarized Exposure. Next, when a pMAzCN film was irradiated with linearly polarized 436 nm light from the surface normal, we observed a relatively large difference in the polarized absorption spectra between parallel-with and perpendicular-to the polarized light irradiation. To compare with the photodichroism induced by nonpolarized exposure (DR_{NPL}), the dichroic ratio induced by the linearly polarized light irradiation (DR_{LPL}) is defined here as

$$DR_{LPL} = (A_\perp - A_{\parallel})/A_0 \qquad (2)$$

where $A_\perp$ and $A_{\parallel}$ are the maximum absorbances of the azobenzene monitored by the probing light with the electric vector perpendicular to and parallel with the polarization plane of the linearly polarized actinic light, respectively. The DR_{NPL} and DR_{LPL} values are compiled in Table 1. After linearly polarized exposure, the DR_{LPL} value was 0.14, about three times larger than the DR_{NPL} of 0.04. Subsequent annealing treatment at 240 °C also enhanced the DR_{LPL} value, raising it to 0.48. The results suggest that the polarized exposure of pMAzCN film gives rise to predominantly azimuthal, highly ordered orientation of the azobenzenes, when compared with oblique nonpolarized exposure.

3.2. 3-D Azobenzene Orientation in pMAzCN Film. To confirm the three-dimensional orientation of azobenzenes induced by photoirradiation, we measured a spatial dichroic ratio (DR_{3D}) as a function of incident angles (θ_m) of probing light, as depicted in the inset of Figure 2A. Here, the DR_{3D} value is here defined as the following equation

$$DR_{3D} = (1 - T_p)/(1 - T_s) \qquad (3)$$

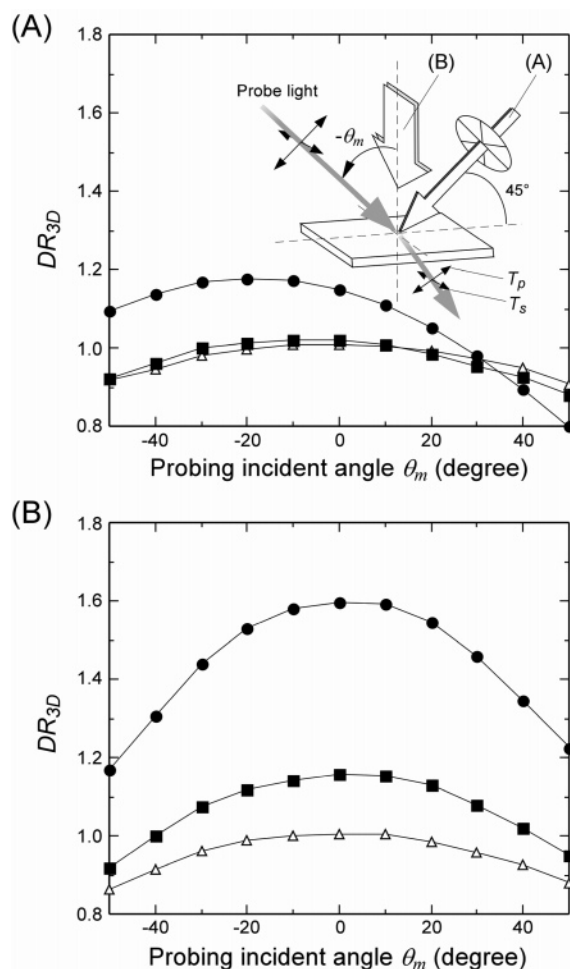where T_p and T_s stand for transmission at maximum wavelength

Figure 2. Changes in the DR_{3D} of pMAzCN films, exposed obliquely to nonpolarized light at an incident angle of 45° (A) and linearly polarized light from the normal (B), as a function of the incident angle (θ_m) of the monitoring light. The energy dose of each exposure was 3.0 J cm^{-2}. The open triangles, closed squares, and closed circles correspond to the pMAzCN film before photoirradiation, after photoirradiation, and subsequent annealing treatment, respectively. Inset (A): experimental configuration for the photoirradiation of pMAzCN film with either oblique nonpolarized light or linearly polarized light from the surface normal. θ_m denotes the incident angle of the monitoring light with either *p*- or *s*-polarization from the surface normal.

attributable to $\pi-\pi^*$ transition of the chromophore when *p*-polarized (electric vector perpendicular to the film surface) and *s*-polarized (that parallel to the surface) are used as probing light at θ_m, respectively. Because the transition moment of the chromophore lies approximately in parallel with its longitudinal molecular axis,[21] this spectroscopic analysis employed here was considered to be most appropriate for elucidation of the spatial orientation of azobenzenes in the polymer film.

Figure 2A indicates the DR_{3D} values of pMAzCN film exposed to oblique nonpolarized light, as a function of the probing light's incident angle, θ_m. Before irradiation, a symmetrical profile of DR_{3D} values with a maximum of $\theta_m = 0°$ was observed (open triangles), indicating that no orientational ordering of the azobenzenes existed at the polar angle. This symmetrical DR_{3D} profile resulted from differences in the reflectance ratio between *p*- and *s*-polarized probing light at larger incident angles. For instance, reflection portions of 0.01% and 13% at $\theta_m = 50°$ were calculated, respectively, for *p*- and *s*-polarized light according to the Fresnel equation, so that $(1 - T)$ involved two factors: the absorption of azobenzene chromophore and the reflection of probing light. When the

profile of the DR_{3D} values before irradiation is corrected taking account of reflection of the *p*-polarized and *s*-polarized monitoring light, the asymmetric curve broadens. This indicates either that in-plane orientation of the azobenzene moieties in the pMAzCN film had already taken place after spin-coating or that the spectral analysis contained experimental error due to multiple reflections. Since we cannot determine at present which of these played the predominant role, the original experimental data is shown here.

When the film was obliquely illuminated with nonpolarized 436 nm light at a dose of 3.0 J cm^{-2}, the maximum DR_{3D} shifted slightly to $\theta_m < 0°$ (Figure 2A, closed squares). Moreover, after the photoirradiated pMAzCN film was annealed at 240 °C for 30 min, the asymmetrical DR_{3D} profile was amplified. The maximum of DR_{3D} value clearly appeared at $\theta_m = -20°$ (closed circles). This indicates that the azobenzene moieties were inclined toward the nonpolarized light propagation of with a pretilt angle of about 20° or less, which is defined as the polar angle between the longitudinal molecular axis of the azobenzene and the substrate surface. The oblique illumination with nonpolarized 436 nm light brought about three-dimensional molecular ordering of the azobenzene chromophores, which in turn led to photodichroism controlled in both polar and azimuthal angles through the subsequent annealing treatment. Furthermore, we found that inclined alignment of the pMAzCN film was also achievable by combining oblique irradiation utilizing nonpolarized 365 nm light to enrich the *Z*-isomer with subsequent annealing treatment. Annealing recovered the *E*-isomer, indicating that the optical anisotropy generated in the *Z*-isomer was memorized and enhanced by the thermal relaxation. Absorption measurements of the pMAzCN film after the annealing treatment revealed the formation of H-aggregates with blue-shifted λ_{max}— due to the $\pi-\pi^*$ transition of the *E*-azobenzene—which stabilized the uniaxially photoaligned state toward thermal stimulus. Such thermal stability of photoinduced tilt alignment is required for the surface-assisted alignment control of DLCs on pMAzCN film, as described below.

The pMAzCN film was also irradiated with linearly polarized 436 nm light from the surface normal, with very contrasting resulting. As seen in Figure 2B, the DR_{3D} values at every incident angle increased while maintaining a symmetrical profile (closed squares). As a result of the subsequent annealing treatment, the DR_{3D} values were intensified while preserving the profile shape (closed circles). The maximum DR_{3D} angle was achieved at the probing incident angle of $\theta_m = 0°$ with the combination of polarized photoirradiation and annealing treatment. Considering the overall results, the perpendicular irradiation of pMAzCN film with linearly polarized light generated only azimuthal reorientation of the *p*-cyanoazobenzenes, whereas oblique nonpolarized light irradiation was able to regulate both their azimuthal and polar angle orientation.

The photoaligned state of the pMAzCN film must be stable toward external stimuli including not only heat, but also solvents, since in order to direct the orientation of the DLC molecules, a DLC solution was to be spin-coated on the pMAzCN film, as to be described later. We found that the chemical stability of the DR_{NPL} to organic solvents was strongly dependent on the annealing temperature after photoirradiation. When the photoirradiated pMAzCN film was annealed at temperatures below 130 °C, the DR_{NPL} values decreased abruptly after immersing the film in organic solvents such as hexane with nonpolarity and 4-methyl-2-pentanone with polarity. In sharp contrast, the combination of photoirradiation and subsequent annealing at 240 °C ensured photoaligned azobenzenes highly stable toward

both heating treatment and organic solvents. This stable orientation was achieved by the extraordinary enhancement of the photoinduced orientation of rigid and polar *p*-cyanoazobenzenes by H-aggregation attained through annealing treatment above the T_g.[15] Thus, the pMAzCN film annealed at 240 °C was deemed most suitable for the surface-mediated orientation of DLCs.

3.3. Orientation Behavior of Discotic Liquid Crystals.
3.3.1. DLC Cell between Two pMAzCN Films. Our first attempt to control the orientation of discotic liquid crystals (DLCs) was by fabricating antiparallel LC cells with pMAzCN films in a manner similar to that for conventional CLC cells.[23] C_8OBzTp in its isotropic phase at 250 °C was placed between two pMAzCN films which had been exposed to oblique nonpolarized light before the fabrication of the DLC cell. As the isotropic fluid was gradually cooled, the optical texture of the C_8OBzTp was observed by polarized optical microscope under crossed polarizers. The Schlieren texture of the N_D phase emerged at 240 °C, followed by the abrupt disappearance of optical birefringence even in N_D phase at 235 °C. Conoscopic observation and pretilt angle measurement of the DLC cells confirmed the inclined homeotropic alignment of C_8OBzTp with a pretilt angle of ca. 89°. When the pMAzCN film was perpendicularly exposed to linearly polarized light, we observed the complete homeotropic orientation of the DLCs. These experimental results indicate that the DLC molecules between two substrate surfaces were strongly anchored on the polymer surfaces and had intrinsically homeotropic orientation.[4a]

3.3.2. Spin-Coated DLC Film on a pMAzCN Film. Next, a spin-coated DLC film with an air-free interface was fabricated according to the following procedure in order to examine the DLCs' photoalignment behavior.[24] A pMAzCN film was irradiated obliquely with nonpolarized 436 nm light with a 3.0 J cm^{-2} dose at an incident angle of 45° and then annealed at 240 °C for 30 min. Next, a DLC film of ca. 1 μm in thickness was prepared on the surface of the pMAzCN film by spin-coating a 20 wt % solution of the C_8OBzTp in 4-methyl-2-pentanone.

Polarized microscopic observation of the DLC film confirmed that its initial polycrystalline texture at 20 °C, due to its crystalline phase, was converted into the fan focal conic texture of the discotic columnar (Col) phase when heated at 160 °C. Further heating at 170 °C brought forth the Schlieren texture of the N_D phase, followed by the disappearance of all optical defects within approximately 10 min, eventually generating the clear optical birefringence of oriented N_D phase. The emergence of the optical anisotropy at N_D phase suggests that the C_8OBzTp molecules oriented in homogeneous or tilted way with respect to the substrate surface. When the oriented DLC film was quickly cooled to room temperature by placing it on an iron plate at 20 °C, the oriented birefringence of the film was retained without crystallization. After 10 months and longer under ambient conditions, a monodomain structure with an excellent optical anisotropy was observed in the DLCs even though no covalent cross-linking reaction had been performed for them. This was accounted for by the formation of a glassy N_D state at room temperature. It is well-known that glassy films of low-molecular weight cholesteric CLCs are achievable through the same rapid cooling procedure despite the absence of any covalent cross-linking reaction.[25] A photoaligned DLC film was also obtained using C_7OBzTp instead of C_8OBzTp. Thus, it was demonstrated that an oriented DLC texture with clear optical anisotropy could be conveniently immobilized through rapid cooling from the N_D phase. The azimuthal orientation of the
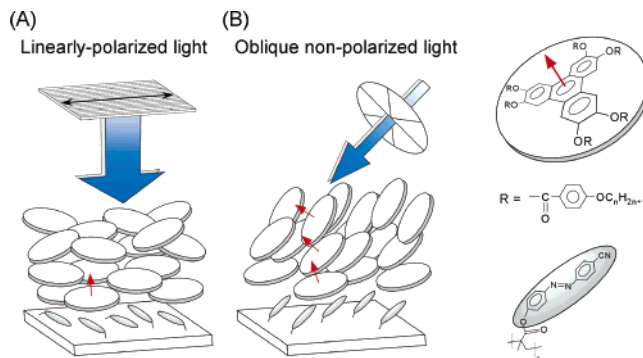

Figure 3. Illustrative representation of the photocontrolled DLC orientation by pMAzCN film.[14] Homeotropic (A) and tilted alignment (B) of the DLCs (denoted as disks) at the N_D phase on a thin film of pMAzCN with *p*-cyanoazobenzene residues (denoted as elliptical rods) exposed either perpendicularly to linearly polarized light or obliquely to nonpolarized light and, respectively. The red arrows indicate the orientational director of the DLC molecules.

oriented glassy DLC film was studied by birefringence measurements using a transmission ellipsometry. Negative minimum values for optical retardation appeared in parallel with the incident plane of the actinic nonpolarized light (see the Supporting Information). These optical results showed that the azimuthal orientation director of the DLC molecules was in parallel with the incident plane of the actinic light propagation due to the negative value of the optical anisotropy (Δn), that is $n_e < n_o$.

On the other hand, a pMAzCN film that was irradiated with linearly polarized light from the normal and annealed in a similar manner exhibited no ability to induce DLC alignment, even though the photodichroism of the pMAzCN film induced by the linearly polarized exposure was much higher than that induced by oblique nonpolarized exposure ($DR_{LPL} = 0.48$ and $DR_{NPL} = 0.16$, respectively, in Table 1). Azimuthal birefringence measurement and conoscopic observation showed that the pMAzCN film irradiated with the linearly polarized light-induced homeotropic alignment with the orientational director of C_8OBzTp perpendicular to the substrate plane, similar to the cases of a nonirradiated pMAzCN film or a hydrophilic silica substrate, as depicted in Figure 3A.[4a,14]

It is worth noting that the perpendicular irradiation of the pMAzCN film with linearly polarized light resulted only in azimuthal reorientation of the *p*-cyanoazobenzenes, while the oblique nonpolarized light irradiation regulated both their azimuthal and polar angles.[18,23] The azimuthal order level of the aligning film was not an important factor for the surface-mediated DLC orientation. The overall experimental results suggest that the following two prerequisites must be fulfilled for optimum generation of DLC photoalignment: first, three-dimensional orientation of the azobenzene side chains should be achieved by oblique nonpolarized light irradiation, as illustrated in Figure 3B,[14] and second, their photoaligned states should be stable to external stimuli, particularly to solvents for spin-coating the DLC solution and heat for generating the N_D phase. The poly[4-(4-cyanophenylazo)phenyl methacrylate] (pMAzCN) employed in this study was deemed most suitable for the photocontrolled orientation of DLC molecules.[14]

3.3.3. Photoaligned Columnar Structure. We were able to make use of the fact that C_8OBzTp showed Col phase below the N_D temperature to form well-aligned columnar-structured DLCs on the pMAzCN film. C_8OBzTp with oriented columnar structure was prepared by first assembling an oriented DLC film of C_8OBzTp at the N_D phase and then slowly decreasing the
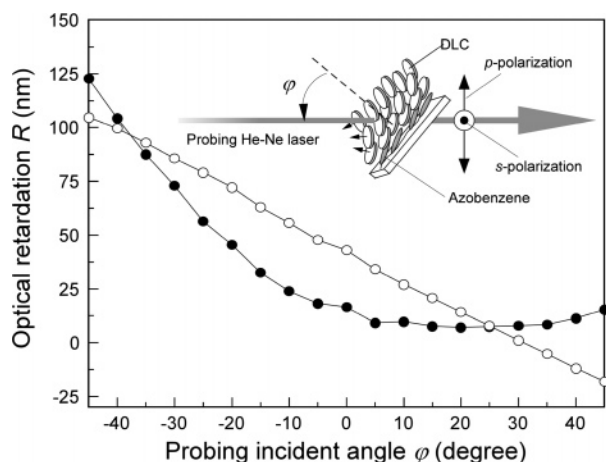
Figure 4. Optical retardation (R) values in nanometer units of two spin-coated C_8OBzTp films on photoaligned pMAzCN thin films, which were exposed to obliquely nonpolarized light and subsequently annealed at 240 °C in advance, as a function of the incident angles (φ) of the probing He−Ne laser beam.[14] The optical profiles were measured at 187 °C (closed circles: N_D phase) and at 25 °C after rapid cooling (open circles: glassy N_D state). Inset: experimental setup for birefringence measurements of a photoaligned DLC film by rotation with respect to the surface normal. φ indicates the incident angle of the probe light with respect to the surface normal of the film.

temperature to 160 °C where the Col mesophase emerged. Under crossed polarizers, the DLCs were observed at this stage to have clear optical birefringence and bundle-like texture (see the Supporting Information). Adam et al. have reported that a 2,3,6,7,10,11-hexahexylthiotriphenylene can exhibit high mobility for photoinduced charge carriers at the helical columnar phase and shows nematic-like mesophase above the helical columnar phase.[4a] Accordingly, our photoalignment procedure described here to form well-organized columnar-structured DLCs through the N_D phase might be applied to fabricate highly anisotropic photoconductive films for nanoelectronic devices.

3.4. Optical Evaluation of Aligned DLC film. To elucidate the spatial orientation director of the photoaligned C_8OBzTp film, we measured optical retardation (R) as a function of the incident angle (φ) of a probing He−Ne laser beam at 633 nm.[26] The experimental setup is depicted in the inset of Figure 4. Figure 4 shows the changes in optical R value in the nanometer unit of two photoaligned DLC films: one of the N_D phase at 187 °C (filled circles) and the other of a glassy N_D state at 25 °C after rapid cooling (open circles). The optical profiles of both of the photoaligned DLC films were asymmetrical with respect to the surface normal, indicating that the oblique nonpolarized light irradiation led to the tilted DLC orientation. The optical birefringence titled to the opposite direction of the *p*-cyanoazobenzenes of the pMAzCN film. The average pretilt angle of the DLC director was estimated to be approximately 78° from the substrate plane by birefringence measurements taking Snell's law into account. Considering the fact that the orientational director of a DLC molecule is perpendicular to the π-extended plane of C_8OBzTp, the inclined birefringence observed for the photoaligned DLC film indicates that at the N_D phase the DLC molecules were aligned in a hybrid manner with continuous alteration of the DLC directors. This was because no optical axis of the DLC film was emerged. It is conceivable that the directors of the DLC molecules are gradually altered within the DLC film so as to minimize the elastic free energy at the outermost region closest to the surface of the DLC film, as illustrated in Figure 3B.[14] The pretilt angle at the interface of air/DLC film was estimated to be 70°, while

the DLC molecules were anchored with a pretilt angle of 88° on the photoaligned film surface of pMAzCN by the theoretical simulation. The pretilt angle was not affected by the conditions of the oblique nonpolarized illumination including wavelengths, exposure doses and incident irradiation angles. The three-dimensional orientation of the DLC molecules was strongly governed by the peculiar features of the photoalignment polymer films such as the surface free energy. Additionally, it was found that the surface-mediated photoalignment of DLC film was achievable by oblique irradiation of a pMAzCN thin film with nonpolarized 365 nm light instead of 436 nm light. The inclined optical profiles obtained were similar to those in Figure 4. Polarized microscope observation indicated that there was only a slight difference between the optical profiles of the photoaligned DLC films of the N_D phase and of the glassy N_D state, as seen in Figure 4. The inclined DLC alignment was partially preserved even after the rapid cooling. The above results and discussion were preliminarily presented in our previous report.[14]

3.5. XRD Measurement of Aligned DLCs. XRD measurement of the DLC films was carried out in order to explain the difference in the optical profiles. The pMAzCN film exhibited no Bragg peak contributing to the XRD patterns of the photoaligned DLC films. Next, we measured the small-angle XRD patterns of oriented glassy DLC films (see the Supporting Information). The Bragg peaks of C_7OBzTp and C_8OBzTp at the low-angle region of 2θ were 3.9° and 3.7°, respectively, indicating that the DLC molecules formed microscopic columnar structures whose diameters were calculated to be 22.6 Å and 23.9 Å, respectively, according to the Bragg's equation. These diameters were smaller than the stimulated molecular diameters of the DLCs, i.e., 27 Å for C_7OBzTp and 30 Å for C_8OBzTp, obtained by the semiempirical molecular orbital calculation (MOPAC), and were probably due to the molecular sliding with respect to each DLC at N_D phase. In addition, the diffraction pattern of C_7OBzTp showed two slight shoulders at $2\theta = 3.7°$ and 4.2°. The C_7OBzTp molecules might form another ordered lattice such as crystalline structure. At the wide-angle region of 2θ, the XRD pattern was very broad and had a very low intensity around $2\theta = 23°$. This derived not only from the peaks of the glass substrate, but also from the distances between neighboring triphenylene cores. It cannot be distinguished here whether the peak appears predominantly around these wide angles. These results indicate that the DLC molecules could not preserve the complete glassy state of the N_D phase at room temperature after rapid cooling from the N_D phase, which resulted in the formation of microscopic ordered domains of discotic columnar or crystalline structures, that is, a pretransitional local order, as supported by previous reports.[27]

XRD pole diagram measurement of the DLC films was conducted in order to elucidate the azimuthal orientational direction in microscopic scale. The experimental setup is illustrated in Figure 5A. Ψ and Φ indicate, respectively, the polar angle from the surface normal and the azimuthal angle from the incident plane of the irradiated nonpolarized light. In this study, we defined the angles of $\Psi = 0°$ and $\Phi = 0°$ when the exposure direction of the X-ray was parallel with the azimuthal orientation director of the photoaligned DLC film. Figure 5B shows the pole XRD diagram of the diffraction intensities of a photoaligned C_8OBzTp film at $2\theta = 3.7°$. A prominent feature of the XRD pattern was its apparent split at large Ψ angles. The direction of the columnar-structured DLCs was prolonged in parallel with the oblique irradiation. These results are very similar to those obtained with an oriented hexakis(4-hexyloxybenzoyloxyl) triphenylene film at the N_D
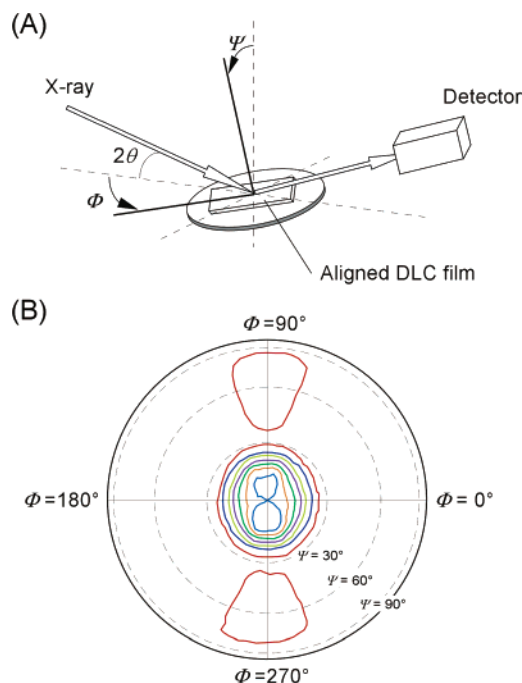
Figure 5. (A) Experimental setup for pole XRD measurements of photoaligned DLC films. Ψ and Φ correspond, respectively, to the polar angle from the surface normal and the azimuthal angle from the azimuthal orientational director of the aligned DLCs in the film. The 2θ of C_7OBzTp and C_8OBzTp were set at 3.7° and 3.9°, respectively, to obtain the maximum diffraction peak. (B) Pole XRD diagram of a photoaligned C_8OBzTp film. The inner, middle, and outer dashed circles correspond to $\Psi = 30°$, 60°, and 90°, respectively. The XRD intensities increased according to the red, blue, yellow, violet, green, orange, and sky blue circles, in that order.

phase under applying an external magnetic field.[27] A similar pole XRD diagram was observed for a photoaligned C_7OBzTp film. The XRD measurements reveal that as consequence of the rapid cooling process from the N_D phase, at room temperature the DLC molecules probably oriented locally in a discotic columnar or crystalline formation with the azimuthal direction parallel with the incident light plane. It was concluded that the slight modification of the optical profile seen in the glassy N_D state, as shown in Figure 4, probably occurred because microscopic molecular assemblages such as discotic columnar or crystalline structures partially formed after rapid cooling from the N_D phase.[27]

3.6. Fluorescence Study on DLC Molecular Arrangement. Fluorescence spectrum measurements of photoaligned DLC film provide invaluable information concerning its molecular aggregation states as well as the spatial orientation of the DLC molecules at the molecular level. It is a highly sensitive analysis technique to elucidate the intermolecular interaction between aromatic chromophores in the microscopic environments, which give rise to intrinsic emission species, such as excimers or intermolecular ground-state complexes, related to molecular arrangement.

The absorption spectrum of C_8OBzTp in a THF solution exhibited an absorption band at 280 nm with a molar absorption coefficient of 2.1×10^5 mol^{-1} dm^3 cm. Accordingly, fluorescence spectrum measurements were carried out by excitation at the absorption maximum absorption wavelength of 280 nm. The fluorescence spectral shape was strongly dependent on the concentration of the DLC solution (see the Supporting Information). In a dilute solution of 2.0×10^{-6} M, the C_8OBzTp exhibited an emission peak at 375 nm, and its fluorescence excitation spectrum monitored at 375 nm had a shape similar
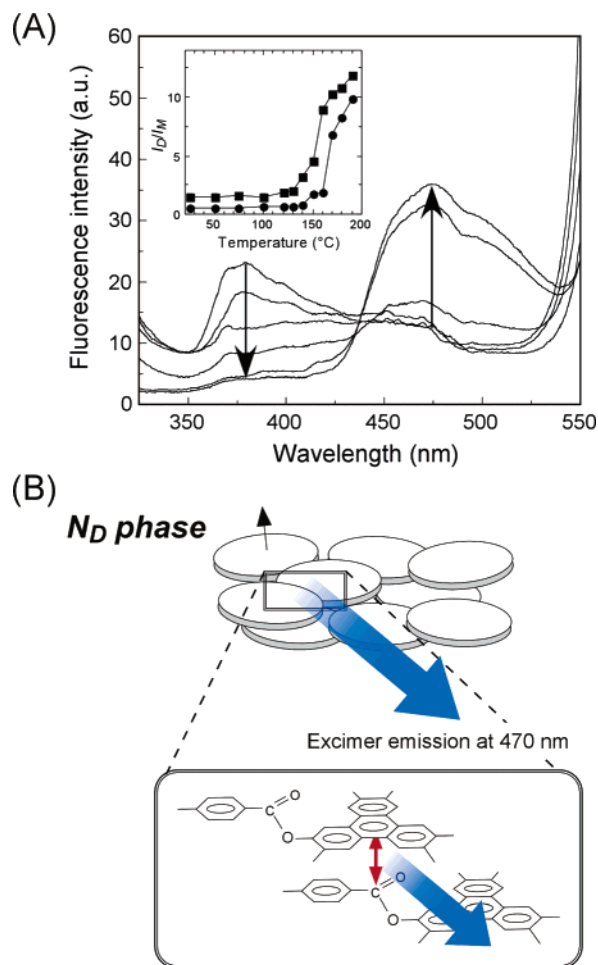

Figure 6. (A) Changes in fluorescence spectra of a DLC film of C_8-OBzTp upon heating at 25, 100, 140, 160, 170, and 190 °C according to the arrows. The fluorescence spectra were measured by excitation at 280 nm. Inset: The I_D/I_M ratio of DLC films of C_7OBzTp (squares) and C_8OBzTp (circles) as a function of temperature increase. I_D and I_M indicate, respectively, excimer fluorescence intensity at 480 nm and monomer fluorescence intensity at 380 nm for the DLCs. (B) Schematic illustration of the molecular arrangement of the DLC molecules at the crystalline state (top) and N_D state (bottom).

to its absorption spectrum. Thus, the fluorescence peak at 375 nm was attributable to monomer emission. When the concentration was increased to 1.0×10^{-3} M, the fluorescence spectrum showed an emission at 420 nm with a shoulder at 375 nm. The fluorescence excitation spectrum of the concentrated solution monitored at 375 nm was not in accord with that monitored at 420 nm. This indicates that the fluorescence emission band at 420 nm did not originate from an excimer but was due to the emission from an intermolecular ground-state complex, that is, a preformed excimer, even in the isotropic medium of the concentrated solution.[28]

Figure 6A shows fluorescence spectral changes of a C_8OBzTp film with 100 nm thickness as a function of temperature increase. A main fluorescence band at 370 nm with a shoulder around 480 nm was observed for the as-coated DLC film. Upon heating, the emission peaks markedly broadened and red-shifted by the changes in the intermolecular arrangement of the DLCs. When the film was heated to its N_D phase at 170 °C, the monomer emission intensity at 370 nm drastically decreased to give a new broad emission band around 470 nm. This indicates that the monomeric structure of the crystalline state DLCs was altered by the partially overlapping molecular arrangement of each DLC plane at the N_D phase. Thus, a photophysical process

such as energy migration might have taken place in the DLC film heated at the N_D phase. The broad emission band at 480 nm resulted from strong intermolecular interaction (electronic distribution change) between the benzoate ester and the triphenylene moieties, which was arisen from the sliding of the molecular arrangement with respect to neighboring C_8OBzTp molecules, as illustrated in Figure 6B. Similar results were observed by Horie et al. for thermotropic calamitic liquid crystalline polymers containing 4,4′-biphenyldicarboxylate moieties.[28b,29] To obtain further information on this molecular interaction, the fluorescence and excitation spectra of the DLC film were measured by wavelengths variant for excitation and emission. The shapes of the fluorescence spectra were independent of the excitation wavelength, whereas the fluorescence excitation spectra depended strongly on the emission wavelength. Despite distortion by self-absorption and multiscattering effect, the fluorescence excitation spectra monitored at 480 nm showed a new broad band around 310 nm after heating at N_D phase. The alterations in the fluorescence spectra of DLC film during heating are attributed to the changes in the intermolecular arrangement of not only the excited state, but also the ground state of the C_8OBzTp.[28a,29]

The ratio of the fluorescence intensity at 470 nm (excimer fluorescence, I_D) to that at 380 nm (monomer fluorescence, I_M), that is, I_D/I_M, was estimated as a function of temperature in order to quantitatively evaluate the overlapping formation of the DLC molecules at microscopic scale. The inset of Figure 6A indicates changes in I_D/I_M for C_7OBzTp and C_8OBzTp induced by heating the DLC film. As is evident from this figure, at the N_D phase the DLCs preferentially exhibited excimer formation. Calamitic low-molecular-weight[30] and polymeric liquid crystals[28a,29,31] showed similar behavior with excimer formation predominantly at the nematic phase. The I_D/I_M ratio of C_8OBzTp abruptly increased at approximately 150 °C, probably due to Col formation, whereas C_7OBzTp exhibited continuously increasing I_D/I_M coinciding with the temperature elevation. The formation of molecular ground-state complexes owing to overlapping between the DLC molecules was clearly ascertained by the fluorescence spectral measurements. The increase in temperature promoted interaction of the intermolecular ground-state complexes. Overall, these experimental results suggest that the phase transition of the DLC molecules might have induced microscopic changes in the molecular arrangement of the DLC molecules, due to the intermolecular interaction between the triphenylene cores. These changes in molecular arrangement became amplified to manifest macroscopically as optical textures. More detailed fluorescence analysis confirmed that the aggregated structures of the DLCs at the substrate interface were decoupled to give their monomeric state as a result of the anchoring transition induced by contact with the pMAzCN film (see Supporting Information).

3.7. Polarized Fluorescence from Aligned DLCs. Further insight into the microscopic ordering of the photoaligned DLCs localized at the outermost interfacial region was provided by polarized fluorescence spectrum measurements. The fluorescence intensity depended significantly on the azimuthal angle of the excitation light. Maximum fluorescence intensity was observed when the excitation was carried out from a direction parallel with the orientation of the DLCs, as depicted in Figure 7A. The results suggest that the DLCs, even at the outermost region closest to the surface, tilted preferably in the opposite direction of the actinic nonpolarized light, as illustrated in Figure 3B. Figure 7B shows polarized fluorescence spectra of a photoaligned glassy film of C_8OBzTp under nonpolarized 280
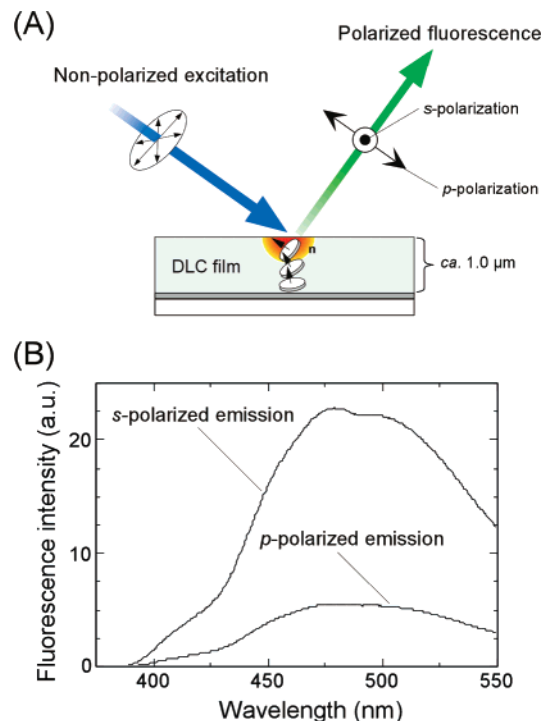

Figure 7. (A) Experimental setup for polarized fluorescence spectrum measurements of a photoaligned DLC film. (B) Polarized fluorescence spectra of a photoaligned DLC film of C_8OBzTp obtained by excitation with nonpolarized 280 nm light in parallel with the orientational director of the tilted DLCs.

nm excitation,[32] where the incident angle of the excitation light was set at 20° from the normal to be in line with the average pretilt angle of the DLCs. Even though the C_8OBzTp was a two-dimensional symmetrical molecule, polarized fluorescence with the predominant electric vector parallel with the DLC plane was observed by the excitation with nonpolarized light at 280 nm,. The s-polarized fluorescence intensity at 470 nm was much larger than the p-polarized intensity, as shown in Figure 7B. To quantify the anisotropic emission characteristics of the oriented DLC film, the dichroic ratio, defined as Em_s/Em_p, was estimated. Em_s and Em_p stand for the intensity of the s- and p-polarized fluorescence, respectively. The fluorescence anisotropy of the photoaligned DLC film on the pMAzCN film ($Em_s/Em_p = 4.1$) was higher than that of an oriented DLC film on a rubbed poly(vinyl alcohol) film ($Em_s/Em_p = 2.6$). Furthermore, we obtained a clear photopatterned fluorescence image to visualize the polarized fluorescence by using pentakis-[(4-alkylphenyl)ethynyl]benzene, which has a high fluorescence quantum yield of approximately 0.6 in the solution.[33,34] The three-dimensional ordering of the pMAzCN film was amplified to the tilted DLCs in the film with approximately 1.0 μm thickness through molecular harmonization arising from the liquid crystallinity, resulting in the polarized fluorescence from the photoaligned DLCs at the outermost region closest to the surface.

3.8. Photocontrol of Patterned DLC Orientation. A prominent advantage offered by our LC photoalignment technique is its capacity to fabricate an orientation-controlled, photopatterned DLC film at microscopic scale, which should make possible novel insights in both fundamental and practical research. We fabricated an orientation-controlled and photopatterned DLC film in micrometer scale according to our previous procedures.[14,24] Briefly, a whole area of a pMAzCN film surface was obliquely irradiated with nonpolarized 436 nm light from *Light-1*, followed by oblique photoirradiation from
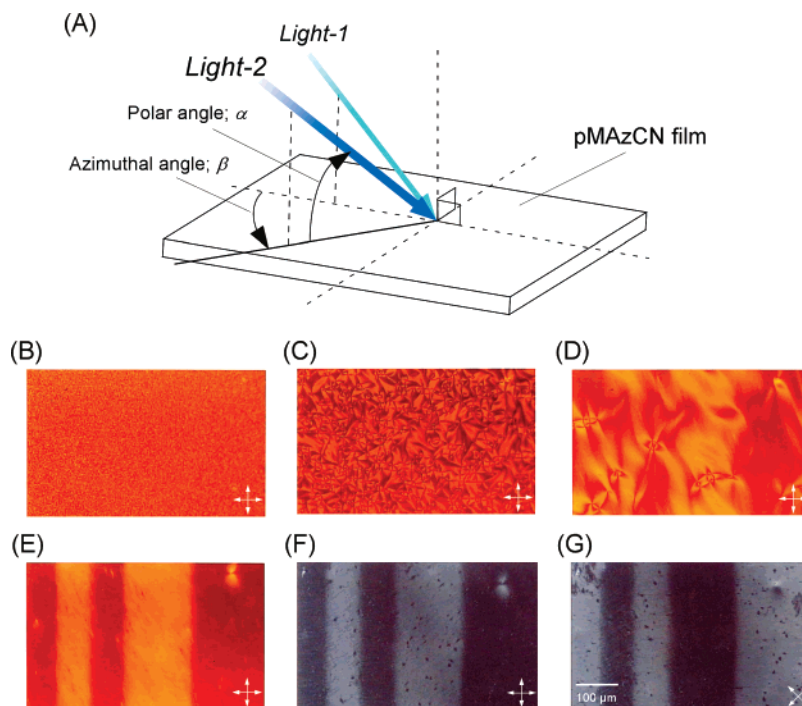
Figure 8. (A) Illustration of oblique irradiation of a pMAzCN thin film with nonpolarized light at polar (α) and azimuthal (β) incidence angles for the photopatterned alignment of azobenzene groups on the polymer surface. *Light-1* and *Light-2* correspond to the propagating direction of α = 45°, β = 0° and of α = 45°, β = 45°, respectively. Polarized micrographs of a C$_8$OBzTp film on a photoaligned pMAzCN film heated at 155 °C (B), 172 °C (C), 174 °C (D), and 176 °C (E) upon heating, respectively.[14] The white arrows in the images indicate the optical axis of the crossed polarizers in the polarized microscope. The photographs were obtained by polarized optical microscopy equipped with an orange-colored cutoff filter. Panels F and G show polarized microphotographs of the glassy photopatterned DLC film after storage for 3 years at room temperature. The photographs were observed by a polarized optical microscopy without any color filters. The polarization axis was rotated 45° between F and G, as shown by the white arrows.

Light-2 through a photomask after rotation of the azimuthal incident direction by 45°, as illustrated in Figure 8A. A C$_8$-OBzTp solution was then spin-coated on the pMAzCN film to obtain a DLC film with thickness of 1 μm.

Polarized microscope observation of the DLC film under crossed polarizers demonstrated that the initial polycrystalline texture at 20 °C was gradually altered by heating treatment to produce a photopatterned image with excellent optical quality formed of oriented DLC film at the N$_D$ phase after passing through the fan focal conic texture of Col phase, as seen in Figure 8B−E. The bright and dark regions of the photoimages seen in the high resolution photoimages correspond to areas of the pMAzCN thin film exposed separately to oblique nonpolarized light with different incident direction, i.e., from either *Light-1* or *Light-2*, respectively. These results were preliminarily presented in our previous report.[14] Furthermore, subsequent rapid cooling of the DLC film to 20 °C preserved the photoimaged mono-domain structures with good transparency in the visible region due to the formation of the glassy N$_D$ state. The photopatterned orientation of the glassy state DLC film was adequately stable when kept at room temperature. It was found that the photopatterned image was still observable on the DLC film after storage for three years, although several defects appeared in the film, as seen in Figure 8F and 8G. The tone of the bright- and dark-striped micrometer-scale photoimages was reversed by rotating the crossed polarizers at 45°, indicating that the birefringence generated in the DLC film clearly resulted from the transfer of the photoaligned azobenzenes by oblique nonpolarized exposure. On-demand control of the DLC director with micrometer-scale spatial resolution can provide valuable opportunities not only to design novel nanodevices for photonics and electronics based on the DLC material, but also to understand fundamental anisotropic physical properties of DLCs at the interfacial molecular level.

4. Conclusion

We have developed a photoalignment strategy to control the orientation of discotic liquid crystals (DLCs) by utilizing an azobenzene-containing polymer thin film. A spin-coated thin film of poly[4-(4-cyanophenylazo)phenyl methacrylate] (pMAzCN) on a silica substrate was obliquely illuminated with nonpolarized light and annealed at 240 °C to induce inclined orientation of the azobenzene chromophores with remarkable thermostability due to strong dipole−dipole interaction among the *p*-cyanoazobenzenes and semicrystallinity of pMAzCN. A solution of DLCs, which show a discotic nematic (N$_D$) phase, was spin-coated on the photoaligned pMAzCN thin film to form a DLC molecular film. Heating this DLC film to N$_D$ phase resulted in the formation of a mono-domain texture. Through subsequent rapid cooling, a glassy state DLC film displayed excellent storage stability even at room temperature for more than three years. The three-dimensional molecular orientation of the DLCs on the photoaligned pMAzCN film was discussed based on ellipsometric, XRD and fluorescence spectrum measurements. The DLC molecules were aligned in a tilted hybrid manner at the N$_D$ phase as a result of the spatial orientation of the *p*-cyanoazobenzenes of pMAzCN film induced by the oblique irradiation with nonpolarized light. Furthermore, optical patterning of the DLC film was achieved by photoirradiation imaging of the polymer film with nonpolarized light. It is anticipated that such DLC photoalignment can be efficiently prepared by utilizing the polarization preserved triplet energy transfer.[35] This report sets forth a general guideline, depicted in Figure 3, to comprehend the orientation mechanism of DLCs

at the molecular level.[14,24,36] Our procedure for the photoalignment of DLCs opens the ways not only to further understanding of detailed anisotropic physical properties of DLC molecules, but also to the design of novel nanodevices for photonics and electronics.

Supporting Information Available: Absorption spectrum changes of pMAzCN film after photoirradiation and subsequent annealing treatment; azimuthal optical phase difference of C$_8$-OBzTp film; well-aligned optical texture of columnar-structured C$_8$OBzTp film; XRD patterns of photoaligned DLC films of C$_7$OBzTp and C$_8$OBzTp; fluorescence spectrum changes of C$_8$-OBzTp in solution; and fluorescence spectral analysis of aligned C$_8$OBzTp at substrate interfaces. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) The polarization-modulating transmission ellipsometer used in this study features high-optical sensitivity due to combining a probing He−Ne laser beam with a photoelastic modulator (PEM). This optical system provides convenient measurement of the optical phase difference angle in degree units (Δ), which represents the difference in optical phase velocity between s- and p-polarized probing He−Ne beam with respect to a DLC film ($\Delta = \Delta_s - \Delta_p$). The optical retardation in nanometric units (R) was estimated according to the equation $R = 633 \times \Delta/360$.

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