

Anchoring Effects of Self-Assembled Monolayers for Polymer-Dispersed Liquid Crystal Films

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Polymer-dispersed liquid crystal (PDLC) films of 4-cyano-4'-pentylbiphenyl (5CB) were fabricated between two quartz substrates, the surfaces of which had been modified with the self-assembled monolayers (SAMs) of $\text{CH}_3-(\text{CH}_2)_{17}-\text{Si}(\text{OMe})_3$ (**1**), $\text{HS}-(\text{CH}_2)_{10}-\text{Si}(\text{OEt})_3$ (**2**), and $\text{NC}-(\text{CH}_2)_{11}-\text{Si}(\text{OEt})_3$ (**3**). The SAM-modification effects on the molecular aggregation of 5CB were investigated by steady-state and time-resolved fluorescence analysis for the PDLC films. Remarkably, it was found that selective excitation of the interface layer with the substrate surface gave both the monomer and excimer emissions of 5CB in relative intensities, depending on the chemical nature of the SAM surfaces. While the monomer and excimer emissions appeared in comparative intensities in the case of the unmodified quartz surface, the surface modification with the SAM of **1** resulted in a dominant contribution of the excimer emission. By contrast, the monomer emission was much stronger than the excimer emission in the case of the surface modified by the SAM of **2**. The surface modification with the SAM of **3** gave a fluorescence spectrum very similar to that in the case of the unmodified surface. Fluorescence decay analysis for the PDLC films revealed that the excimer emission consists of two components with shorter (1.3–1.6 ns) and longer (10–12 ns) lifetimes, whose relative contributions depend on the SAM modifications. The molecular pictures of 5CB depicted from the decay dynamics are in good agreement with those derived from the steady-state fluorescence behavior of the PDLC films. Electrooptic devices based on the PDLC films were constructed by using indium–tin oxide transparent electrodes modified with the SAMs, and it was confirmed that the electrooptic responses again significantly depend on the modifications of the substrate surface. The dependency of the fluorescence and electrooptic behavior on the surface modifications for the PDLC films has been discussed in terms of anchoring effects of the substrate surfaces, which effectively work even in heterogeneous materials such as PDLCs.

Introduction

Heterogeneous thin films of polymer-dispersed liquid crystal (PDLC), which have LC droplets in polymer matrixes, are materials of considerable current interest in scientific fields as well as for electrooptic applications.¹ The fabrication of PDLC films can be conveniently achieved by photopolymerization-induced phase separation (PIPS) of homogeneous LC/prepolymer mixtures sandwiched between two solid substrates.² Devices of PDLC films sandwiched between transparent electrodes can be switched from a light-scattering opaque state to a transparent state upon applying a modest electric field to the electrodes, having been applied to a new type of LC display panels which do not need back light, alignment film, or polarizer.

In general, it is known that orientation of LC molecules is significantly affected by the nature of interfaces in contact with the LC domain, so-called anchoring phenomena.^{3,4} In PDLC films, there are two types of interfaces, one between LCs and polymer matrixes and the other between LCs and substrates. It should be therefore predicted that such interfaces play an important role in the PDLC functions. Interactions of LC molecules with polymer matrixes have been widely investigated since they are one of the major factors for controlling the morphological aspects of PDLC materials.⁵ On the other hand,

little attention has been paid to the significance of interactions between LC molecules and electrode surfaces, probably due to the inherent working mechanism of PDLC devices, which do not need alignment films on electrodes.

We have been investigating the fluorescence behavior of 4-cyano-4'-pentylbiphenyl (5CB) in PDLC films using the *surface-limited excitation* (SLE) and *through-film excitation* (TFE) methods to achieve specific analysis of aggregation features of LC molecules in an interface layer (≤ 60 nm) with the substrate discriminating from those in the interior bulk. It was demonstrated that the interface layer of PDLC films has unique molecular alignments and mobility of 5CB, substantially different from those of the typical 5CB nematic phase extensively distributing in the interior bulk.⁶ Moreover, the obtained results suggest that the unique molecular feature of 5CB in the interface layer should be a consequence arising from a specific interaction of the LC domains with *both* of the polymer matrixes and the substrate surface because such a molecular feature was *not* observed in a neat thin film of 5CB even in the interface layer.^{6b} Taking into consideration these findings that the substrate surface might exert a significant influence on the molecular aggregation in the PDLC films, the surface control of substrates would be expected to potentially operate the net PDLC functions as well.

The self-assembled monolayer (SAM) technique⁷ presents a way for surface control because the chemical tuning of substrate

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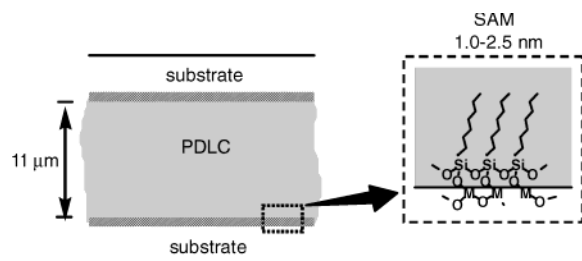


Figure 1. A schematic illustration of PDLC film with SAM-modified substrates (not to scale).

surfaces can be easily achieved while maintaining the defined surface topology (Figure 1).^{8–10} From this viewpoint, we demonstrated in a preliminary communication that the PDLC function could be significantly altered by modifying substrate surfaces with a particular boronate-terminated SAM through its controlled chemical transformation reactions.¹¹ The molecular aggregation feature of 5CB in the interface layer can be widely and systematically tuned depending on the hydroxy-group density of the substrate surface. The preceding work has motivated us to get basic and general insights into the SAM effects on PDLC functions. Hence, we have undertaken to study the steady-state and time-resolved fluorescence behavior of PDLC films that were fabricated with SAM-deposited substrates, the SAMs of which possessed typical chemical termini individually. We wish to report herein that the PDLC films of 5CB reveal unique molecular aggregation manners and intriguing electrooptic performances strongly depending on the chemical nature as well as polarity of the SAM surfaces.

Experimental Section

Materials. 5CB was donated from Dainippon Ink & Chemicals Co. Ltd. and used as received. Octadecyltrimethoxysilane (**1**) (Shinetsu Silicon Chemicals), the diacrylate monomer (Nippon Kayaku), and the photoinitiator (Ciba Geigy Irgacure 184) were used as received. The procedures for the synthesis of 10-mercaptodecyltriethoxysilane (**2**) and 11-cyanoundecyltriethoxysilane (**3**) are reported in Supporting Information. Quartz and indium–tin oxide (ITO)-coated (50 Ω/□) glass substrates (25 × 25 mm², 1.0 mm thick) were used after washing once with Merck Extran MA02 detergent solution and then several times with deionized water in an ultrasonicator bath.

Preparation of PDLC Films. A homogeneous mixture of 5CB, the diacrylate monomer, and the photoinitiator (~1 wt % of the monomer) was sandwiched between two unmodified or SAM-modified substrates with 11 μm thickness and was photoirradiated at ≥310 nm through both sides of the two substrates at 25 °C using a high-pressure mercury arc (2.3 mW cm⁻² at 366 nm) combined with a neutral glass filter and a cutoff glass filter (<310 nm). The weight ratio of 5CB was fixed to 30 or 77 wt %. The quartz or ITO-coated glass substrates were used for fluorescence measurements and electrooptic measurements each.

Fluorescence Measurements. Steady-state fluorescence spectra were obtained on a Hitachi F-4500 spectrofluorimeter. The 30 wt % 5CB PDLC films sandwiched between two quartz substrates were excited with an incident angle of the excitation light beam at 45°, and the fluorescence emitted in a direction orthogonal to the excitation light beam was picked up from the front surface. Details of the measurements are essentially identical to those described in a previous paper.⁶

For the fluorescence-decay analysis, SLE was performed with the fourth harmonic (266 nm, full width at half maximum

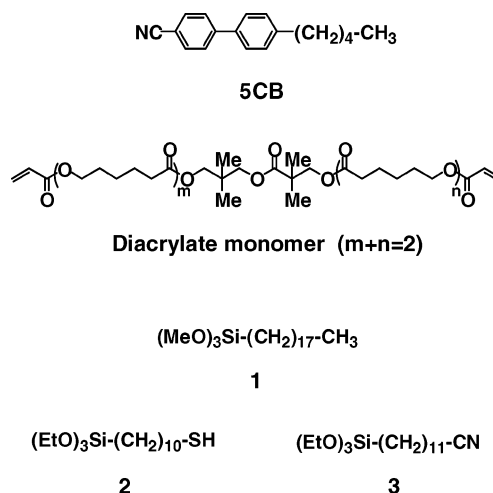


Figure 2. Chemical structures of the compounds used in this study.

(fwhm) 30 ps, 5 Hz) of a mode-locked Nd³⁺–YAG laser (EKSPLA-Tokyo Instruments, PL2143B) and the decay profiles were monitored by a picosecond fluorescence lifetime measurement system (a Hamamatsu C4334 streak scope, connected with a CHROMEX 250IS polychromator). The power density of the excitation laser pulse was set at 1 μJ cm⁻², weak enough to avoid possible multiphoton-induced processes. The decay profiles were monitored at 330 nm for the emission of monomeric 5CB and at 450 nm for the 5CB excimer emission.

Electrooptic Measurements. Optical transmittances through the 77 wt % 5CB PDLC films fabricated between two ITO-coated glass substrates were measured with a photomultiplier as a function of applied 1-kHz sinusoidal voltage at room temperature, through an optical system equipped with a halogen arc.

Results and Discussion

Figure 2 displays chemical structures of the compounds used in this study. We used the alkyltrialkoxysilane compounds (**1**–**3**) having typical chemical termini for modification of substrate surfaces. Although the corresponding alkyltrichlorosilanes are alternative molecules for SAM formation, possible contamination of acidic and/or charged species might occur to cause unexpected effects on the fluorescence and electrooptic behavior of the PDLC films. Octadecyltrimethoxysilane **1** is known as a typical SAM-forming compound capable of lowering the surface free energy, while the alkyltriethoxysilanes with ω-mercapto (**2**) and ω-cyano (**3**) groups can be expected to yield high dielectric environments on the resulting SAM surfaces.

The syntheses of the compounds **1**–**3** and the preparation and characterization of their SAMs are described in Supporting Information.

Steady-State Fluorescence Spectra. PDLC films were constructed by the PIPS procedure for a mixture of 30 wt % 5CB and a diacrylate monomer was sandwiched between unmodified or SAM-modified quartz substrates. For convenience, the PDLC films using unmodified substrates and the substrates modified with the SAMs of **1**, **2**, and **3** are abbreviated as PDLC-A, PDLC-B, PDLC-C, and PDLC-D, respectively.

Figure 3 shows the normalized fluorescence spectra of the PDLC films taken by excitation at 290, 300, 310, 315, and 320 nm. It is well known that excited-singlet 5CB reveals the fluorescence at ~340 nm and, at higher concentrations, competitively forms an excimer which emits at ~400 nm.^{12,13} The monomer and excimer emissions comparably appear for PDLC-A

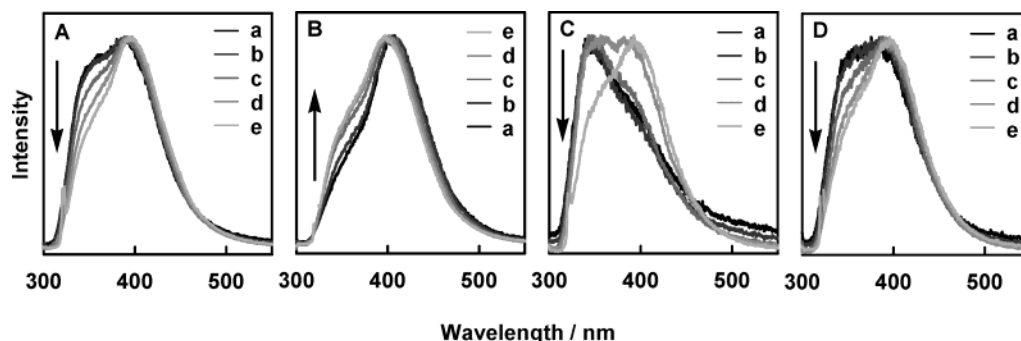


Figure 3. Normalized fluorescence spectra of 30 wt % 5CB PDLC films taken by excitation at (a) 290 nm, (b) 300 nm, (c) 310 nm, (d) 315 nm, and (e) 320 nm at room temperature. The films were sandwiched between two quartz substrates unmodified (A) and modified with the SAMs of **1** (B), **2** (C), and **3** (D).

when excited at 290 nm (SLE), but the latter becomes major with the increase of excitation wavelength (Figure 3A). On the other hand, PDLC-B, with the substrates modified by the long aliphatic SAM, reveals a maximum contribution of the excimer emission when excited at 290 nm and an increase of the monomer-emission intensity with the increase of the excitation wavelength (Figure 3B), behavior opposite to that of PDLC-A. In the case of PDLC-C, by contrast, the modification with the mercapto-bearing SAM gave rise to quite different behavior of the fluorescence such that the monomer emission dominates over the excimer emission in the fluorescence spectrum taken by excitation at 290 nm (Figure 3C). The increase in the excitation wavelength resulted in a drastic spectral change to excimer-rich spectra. Intriguingly, however, the modification with the SAM having the cyanoalkyl group (PDLC-D) exerted little effect on the fluorescence spectra of the PDLC film (Figure 3D), i.e., almost identical with those of PDLC-A, unlike those with the other SAMs.

The excitation–wavelength dependence observed for the steady-state fluorescence spectra of the PDLC films can be explained in terms of the penetration depth of the excitation light beam, as already reported.⁶ The excitation light at 290 nm used for SLE should be completely absorbed by 5CB in a very thin interface layer (≤ 60 nm) due to its extremely high optical density to give the fluorescence from this interface layer. On the other hand, the absorbance of 5CB sharply drops at ≥ 300 nm so that the excitation light can penetrate into a deeper region of the film at longer wavelengths and, finally, can pass through the film at 320 nm (TFE) to give the emission dominantly from the interior bulk.¹⁴

It is therefore reasonable to consider for PDLC-A (Figure 3A) that the excimer formation should be less favorable in the interface layer than in the interior bulk. It has been well documented that the molecular aggregation manner of 5CB and related LCs nicely fits the excimer formation in the nematic phase but is less favorable in the isotropic and smectic A phases.¹³ Accordingly, the fluorescence behavior of PDLC-A strongly suggests that the nematic phase should be dominant in the interior bulk, as expected, but is significantly disturbed in the interface layer, which is probably a consequence of interacting 5CB molecules with the quartz surface.

However, the opposite excitation–wavelength dependence of PDLC-B (Figure 3B) in its fluorescence spectra indicates that the nematic aggregation of 5CB is more notable in the interface layer with the substrate than in the interior bulk. To consider this unique feature of PDLC-B, a well-known anchoring phenomenon of LC molecules is suggested, where an attachment of long aliphatic chains onto the surface generally leads to a decrease in the surface tension to induce a homeotropic

orientation of LC molecules at the surface.¹⁵ It is conceivable that such an orientation effect affords long-range nematic interactions of LCs in the interface region, in which the LC molecules align in a near upright direction against the substrate surface. Analogously, the surface modification with the SAM of **1** is expected to exert a similar effect on the 5CB aggregation in the PDLC films, thereby making the growth of well-developed nematic domains promoted in the interface layer. It is in good accordance with the results previously reported that the boronate SAM modification gave the excimer-dominant spectra in the interface layer of the PDLC film through the second aliphatic layer treatment.¹¹

On the other hand, the extremely monomer rich fluorescence of PDLC-C by SLE (Figure 3C) obviously indicates that the nematic phase is greatly disturbed in the interface region of this film. Interestingly, this fluorescence spectrum is very similar to that of the molecularly dispersed *homogeneous* 5CB/monomer mixture before PIPS (data not shown here).^{6a} It is therefore suggested that the mesogenic interaction of 5CB molecules should be much lessened in the interface layer with the **2**-modified substrate. A strong dipole interaction between 5CB and the surface mercaptoalkyl group appears to occur to suppress the growth of the nematic LC domains in the interface layer.

In the case of PDLC-D (Figure 3D), however, the fluorescence spectra were very similar to those of PDLC-A, indicating little effect of the polar cyanoalkyl groups on the 5CB aggregation. The different effects of the cyano- and mercapto-bearing SAMs can be explained not only by polarity of the end groups of the SAMs but possibly, to a certain extent, in terms of an *acid–base* dispersive interaction between 5CB and surfaces. In this regard, it is significant to note that the cyano group is baselike while the mercapto group is acidlike. Therefore, it can be predicted that 5CB acting as a base should interact more effectively with the acidlike **2**-modified surface than with the baselike **3**-modified one. Frank et al. also pointed out the significance of acid–base interactions in LC anchoring phenomena through the study with systematically designed end-functionalized SAM surfaces.¹⁶

In the previous paper, we demonstrated that the fluorescence spectra of 5CB PDLC films drastically vary depending upon the hydroxy-group density of the SAM-deposited substrate surfaces.¹¹ Taking into consideration the weak but significant proton-donating nature of hydroxy groups, those remarkable effects on the 5CB aggregation are in good agreement with a perspective of the acid–base interactions. In this regard, it should be noted that PDLC-A gives comparable contributions of the monomer and excimer emissions in the interface layer, despite the acidic nature of bare quartz surfaces. This has not been well understood, but it would be reasonable that interac-

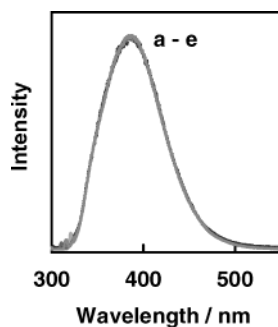


Figure 4. Normalized fluorescence spectra of a neat 5CB film taken by excitation at (a) 290 nm, (b) 300 nm, (c) 310 nm, (d) 315 nm, and (e) 320 nm at room temperature. The film was sandwiched between two bare quartz substrates.

tions of 5CB with the *inorganic acidic surface* of quartz are less effective because of inherent incompatibility of the organic–inorganic interfaces, unlike with the *organic acidic surfaces* of the mercaptoalkyl or hydroxyalkyl SAMs.

It is also of importance to mention that fluorescence spectra of neat 5CB films were *never* influenced by the substrate-surface modifications with the SAMs of 1–3. Figure 4 shows the normalized fluorescence spectra of a neat 5CB film sandwiched between two bare quartz substrates, which exclusively give the excimer emission with no contribution of the monomer fluorescence independently of the excitation wavelengths at 290–320 nm. Indeed, this set of the spectra in Figure 4 is a representative one for all the neat 5CB films, i.e., no change was observed in the fluorescence spectra if the substrates had been modified with any SAMs used in this study. These results clearly indicate that the nematic aggregation of 5CB is not disturbed solely by interaction of 5CB molecules with the SAMs deposited on substrate surfaces. Accordingly, the strong dependency of 5CB aggregation in the interface layer upon the SAM deposition is a unique behavior observed for the PDLC systems. This presumably arises from the cooperative interaction of 5CB molecules with *both* of the polymer components and the SAM surfaces, which was specifically provided through the PIPS process.

When focusing on the interior region of the PDLC films, it is easily realized that the nearly identical excimer-rich spectra were obtained by TFE commonly for all the films as shown in Figure 3 (λ_{ex} , 320 nm). Therefore, the nematic phase should be dominant in the interior domain independently of the surface modification with the SAMs. This feature can be reasonably understood because of the well-established discontinuous phase-separated structure of PDLC films, which involves distinct LC droplets dispersed in polymer matrixes. However, it should be noted that the monomer emission at around 340 nm slightly but significantly contributed to the interior fluorescence spectra equally for all the PDLC films. This is probably due to an interfacial effect for the interior LC droplets, where molecular association in the 5CB droplets should be partially disturbed at the interface with the surrounding polymer matrixes.

With regard to this probable interfacial effect for the interior LC domains, that the fluorescence spectrum by SLE for PDLC-B gave the excimer emission with nearly no contribution of the monomer emission is interesting to consider the 5CB aggregation features in the interface region with the substrates. This fact strongly suggests that the nematic aggregation of 5CB in the interface layer of PDLC-B is not affected by the interfacial disturbance from the polymer matrixes. On the basis of this presumption, it is possible to imagine that the SAMs on the substrate surfaces might affect *relative concentrations and*

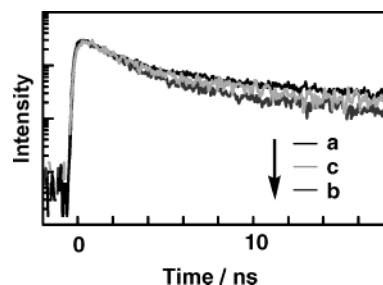


Figure 5. Decay profiles of excimer emission for 30 wt % 5CB PDLC films taken by excitation at 266 nm at room temperature. The films were sandwiched between quartz substrates modified with SAMs of 1 (a), 2 (b), and 3 (c).

TABLE 1: Fluorescence Rise and Decay Components of 30 wt % 5CB PDLC Films^a

film ^b	λ_{em} (nm) ^c	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
PDLC-A	330	0.12 (0.87)	1.0 (0.12)	6.9 (0.01)
	450	0.17 (−0.37)	1.5 (0.55)	12 (0.08)
PDLC-B	330	0.19 (0.89)	1.0 (0.10)	5.1 (0.01)
	450	0.13 (−0.30)	1.5 (0.52)	10 (0.18)
PDLC-C	330	0.21 (0.79)	0.77 (0.20)	4.7 (0.01)
	450	0.60 (−0.29)	1.6 (0.63)	12 (0.08)
PDLC-D	330	0.16 (0.84)	0.95 (0.15)	6.5 (0.01)
	450	0.39 (−0.37)	1.3 (0.53)	10 (0.10)

^a Values in parentheses are the pre-exponential factors. ^b The PDLC films using unmodified quartz substrates and the SAM-modified substrates with 1, 2, and 3 are abbreviated as PDLC-A, PDLC-B, PDLC-C, and PDLC-D, respectively. ^c Emission wavelength to monitor decay profiles.

distributions of the LC and polymer components in the interface region depending on their relative affinities. Further studies along these lines are currently underway.

Fluorescence Decay Dynamics. For the fluorescence-decay analysis of 5CB located in the interface layer, the PDLC films were excited at 266 nm using the fourth harmonic of a mode-locked Nd³⁺–YAG laser (fwhm 30 ps, 5 Hz). The monomer emission was analyzed at 330 nm where the excimer emission is negligible, and the 5CB excimer emission was analyzed at 450 nm where the monomer emission has little contribution. Figure 5 shows fluorescence-decay profiles of the excimer emissions for the 30 wt % 5CB PDLC films with the SAM-modified substrates. The observed time dependence of the emissions was satisfactorily analyzed on the basis of the triple-exponential function, $A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$. Table 1 summarizes the analyzed data for the rise and decay components of the monomer and excimer emissions together with those of PDLC-A.

The decays of the monomer emissions for all the films showed similar characteristics independent of the substrate-surface modifications. The major component of a rapid decay (<210 ps) should be associated with the excimer formation.^{13,17,18} The second ~1-ns component can be attributed, for the most part, to the decay of excited-singlet 5CB that has occurred prior to or without the excimer formation,^{17,18} but another minor contribution may arise from the regeneration of excited-singlet 5CB from the short-lived excimer which is described below.^{6b} The component with the longest lifetime (4.7–6.9 ns) was also observed for all the films, even to a very minor extent. This component is not easy to be assigned to a particular emissive species, but it might be appropriate to assume the participation of an unknown species generated in the interface region of the PDLC films.

The excimer decay profiles also gave a similar trend for all the PDLC films, but, at the same time, a significant difference

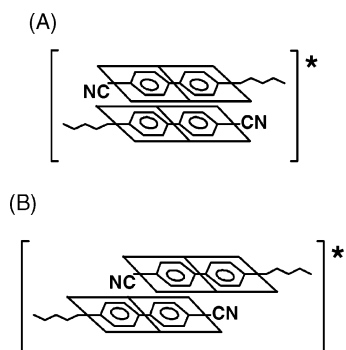


Figure 6. Possible excimer structures of 5CB: (A) a fully overlapped antiparallel arrangement; (B) a partially overlapped antiparallel arrangement.

can be observed depending upon chemical structures of the SAMs deposited on the substrates. The excimer emission of PDLC-A showed a two-phase decaying behavior involving a dominant shorter-lived component (1.5 ns) accompanied by a minor longer-lived one (12 ns). Similarly, for all the SAM-modified films, the excimer emission consists of the major shorter-lived (1.3–1.6 ns) and the minor longer-lived (10–12 ns) decay components following a rapid rise (130–600 ps). The significant difference among the SAM-modified films comes from the relative contribution of the two excimer components compared to that of PDLC-A, i.e., with regard to the longer-lived excimer, a greater contribution for PDLC-B, a comparable one for PDLC-D, but a smaller one for PDLC-C.

Decay behavior of the excimer emission is suggested to examine molecular aggregation features of 5CB in PDLC films with regard to the SAM effects. We previously reported a particular type of two-phase decay behavior consisting of shorter-lived and longer-lived components for the excimer emission in the interface layer of PDLC films and assigned them as excimers of 5CB having different molecular arrangements.^{6b} The longer-lived component of over 10 ns is typical of an excimer having a fully overlapped antiparallel arrangement of the chromophores, which is extensively observed in the nematic phase of 5CB and related alkyl- and alkoxybiphenyl LCs.^{13,17–19} On the other hand, the unusual shorter-lived one with a 1–2-ns lifetime can be attributed to an excimer with a partially overlapped chromophore arrangement,^{6b} which was reported to be formed, even to a minor extent, in the smectic A phase of some cyanobiphenyl LCs having longer alkyl chains than 5CB.^{17,18} That is, the shorter-lived excimer is likely to be generated only in relatively viscous and restricted fields of LC phases. Since 5CB does not form the smectic A phase inherently, the substantial formation of the shorter-lived excimer in the PDLC films indicates that the nematic phase should be partially restricted in motion in the interface layer due to specific interaction with the substrate surface. Plausible molecular arrangements of the 5CB excimers are provided in Figure 6.

Accordingly, 5CB molecules in the interface layer with the **1**-modified substrate relatively prefer to take nematic alignment since the contribution of the longer-lived excimer is relatively large, but 5CB located near the **2**-modified surface, giving relatively large contribution of the shorter-lived excimer, should be restricted in motion probably due to the specific interaction with the mercapto groups. The surface modification with **3** showed little effect on the excimer decay behavior, in which relative contributions of the shorter-lived and longer-lived components are nearly identical with that of PDLC-A. The molecular pictures depicted from these findings, interestingly, are apparently in line with those derived from the steady-state

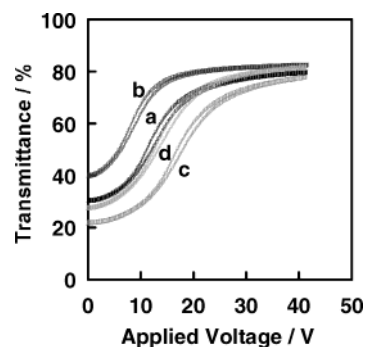


Figure 7. Optical transmittances through 77 wt % 5CB PDLC films versus an applied 1 kHz voltage at room temperature. The films were sandwiched between ITO-coated glass substrates unmodified (a) and modified with SAMs of **1** (b), **2** (c), and **3** (d).

fluorescence behavior. However, it is important to remember that the contribution of the excimer emission, which is paid attention for the present decay analysis, is fundamentally different among the PDLC films, as stated in detail referring to Figure 3.

Instead, to compare the excimer decay dynamics of PDLC-B to that of the neat 5CB film is more useful to understand the SAM effects on the 5CB aggregation in the interface layer. As described above, PDLC-B gave the nearly pure excimer emission in the steady-state fluorescence spectra, which exhibited very similar behavior to that of the neat 5CB sample. However, there is a sharp contrast in the excimer dynamics between them, in which the former gives the two-phase decay behavior consisting of major shorter-lived (1.5 ns) components and minor longer-lived (10 ns) one as shown in Table 1, whereas the latter exclusively shows single-component decay kinetics with a 17-ns lifetime (data not shown here, see ref 6b). This single-component decaying behavior of the excimer emission is independent of the substrate-surface modifications for the neat film, i.e., it is exactly true even for the neat sample modified with the SAM of **1**. Accordingly, the significant appearance of the unusual shorter-lived excimer seems to be a unique behavior for PDLC-B. This can probably be interpreted that the 5CB molecules in the interface layer of PDLC-B are allowed to take nematic aggregation but are also restricted partially in motion under the control of the long aliphatic chains of **1** with the significant assistance of the polymer components, thus giving a *metastable* excimer to a large extent.

Electrooptic Functions. For electrooptic investigation, we constructed PDLC films of 77 wt % 5CB using unmodified or SAM-modified ITO-coated transparent electrodes. The SAM deposition onto ITO surfaces had been performed in a manner essentially identical to that described above. Optical-transmittance responses of the films were measured upon application of 1-kHz sinusoidal voltage using a photomultiplier at room temperature.

As shown in Figure 7, the transmittance–voltage (*TV*) curves for the PDLC films clearly demonstrate that the SAM modification for electrode surfaces gives significant effects on the electrooptic performance. Table 2 summarizes the electrooptic parameters determined from the *TV* curves for the PDLC films. The **1**-modified film shows the largest transmittance value before applying the voltage (T_{\min} , 39.0%) among the films, thereby giving a smaller device contrast (CR, 2.09) compared to the unmodified one (CR, 2.68). However, the **1**-modified film is more susceptible to applied electric field than the unmodified one, as shown by the much higher γ value of the former (4.23; see also the V_{90} value, 18.2 V) compared to that of the latter

TABLE 2: Electrooptic Parameters of 77 wt % 5CB PDLC Films^{a,b}

SAM modification	T_{\min} (%)	T_{\max} (%)	V_{10} (V)	V_{90} (V)	CR	γ
none ^c	29.4 ± 0.4	78.8 ± 0.4	6.7 ± 0.3	24.8 ± 0.2	2.68 ± 0.05	3.69 ± 0.02
1	39.0 ± 0.3	81.8 ± 0.3	4.3 ± 0.3	18.2 ± 0.3	2.09 ± 0.04	4.23 ± 0.03
2	20.8 ± 0.4	77.0 ± 0.4	9.5 ± 0.3	29.5 ± 0.4	3.70 ± 0.05	3.12 ± 0.02
3	26.7 ± 0.4	80.9 ± 0.5	7.0 ± 0.3	25.9 ± 0.3	3.03 ± 0.03	3.69 ± 0.03

^a T_{\min} and T_{\max} are the minimum and maximum transmittance values, respectively, V_{10} and V_{90} the voltages at transmittance of 10 and 90%, respectively, CR indicates the contrast between the minimum and maximum transmittance corresponding to T_{\max}/T_{\min} , and γ represents the susceptibility of the TV responses corresponding to V_{90}/V_{10} . ^b Averaged values for at least three sets of each sample. ^c Bare ITO electrodes.

(3.69; V_{90} , 24.8 V). On the other hand, the SAM modification with **2** leads to different behavior opposite to that of the **1**-modified film, e.g., a high contrast value (CR, 3.70) due to a small T_{\min} value (20.8%) but a slow response upon applying the voltage (γ , 3.12). In the case of the **3**-modified film, all the electrooptic parameters are comparable to those of the unmodified case, demonstrating little effect of this SAM on the PDLC characteristics again.

Interestingly, the molecular-aggregation features of 5CB derived from the fluorescence behavior provide useful indications to consider the SAM effects on the electrooptic properties. A possible interpretation can be made that the 5CB molecules located near the **1**-modified surface should be well ordered to lead to the growth of nematic domains, thereby a cooperative change of the LC orientation might easily occur along the electric field upon applying a relatively modest voltage. When the electrodes are modified with the SAM of **2**, on the other hand, mesogenic interaction of the 5CB molecules should be much less by the interaction with the mercapto groups to lower the molecular mobility, so that the induced molecular disorder of 5CB might result in a high degree of light scattering at the voltage-off state and a slow response against the electric field for the PDLC films. The electrooptic behavior of the **3**-modified film is similar to that of the unmodified one, in line with little effect of the **3** modification on the fluorescence behavior. These presumptions are in good accordance with electrooptic properties of the SAM-modified PDLC films previously reported, in which the electrooptic behavior was discussed mainly in terms of hydroxy-group densities of the SAM surfaces on the electrodes.¹¹

Thus, the present device performances strongly indicate that the substrate-surface modifications can give crucial effects not only for the interfacial properties at the substrate surface but also for overall functions of the PDLC systems. This is particularly interesting when taking into consideration the fact that the LC phase in PDLC films fabricated by photopolymerization is *not* continuous even at high LC content (~80 wt %) but forms spherical LC droplets.²⁰ It can be therefore presumed that the unique molecular aggregation characteristics of 5CB in the interface layer cooperatively affect the molecular feature in the interior LC droplets of the PDLC films. Hence, we speculate that the PIPS process, which is exactly dynamic in nature, can play an important role to magnify the SAM effects across the entire film to a certain extent. The essence of the SAM effects might be to influence relative concentrations and distributions of the LC and polymer domains for the entire PDLC films, depending on relative affinities of the SAMs, thereby leading to different bulk properties associated with the electrooptic functions of the films.

Conclusions

In the present study, we have fabricated the PDLC films of 5CB using the SAM-modified substrates to explore effects of

the surface modifications for the PDLC films. Major findings obtained through the fluorescence analysis and electrooptic measurements for the PDLC films are as follows.

(1) The molecular aggregation manner of 5CB in the interface layer is highly dependent on the chemical nature as well as the polarity of the SAMs deposited onto the substrate surfaces.

(2) The strong dependency of 5CB aggregation on the SAM modification is a unique characteristic for the PDLC films since such behavior is not observed for the neat 5CB films. In other word, nematic aggregation in the neat film is not disturbed solely by interactions of 5CB molecules with the SAMs.

(3) The substrate-surface modification with the SAMs can also give a crucial effect to electrooptic function that can be regarded as one of the important *bulk* properties of the PDLC films.

All the characteristics listed above strongly suggest that the nature of substrate surfaces can intrinsically play an important role for the PDLC systems. That is, the molecular anchoring at the PDLC–substrate interface exactly works even in such heterogeneous materials as PDLC. It can be stated that this anchoring phenomenon basically results from specific interactions of the 5CB molecules with both of the polymer components and substrate surfaces. We speculate that PIPS should be a key for the surface anchoring, where the substrate surface participates in the event of phase separation between the 5CB LC phases and growing polymer matrixes to give a specific morphology and, possibly, to affect relative concentrations and distributions of the LC and polymer domains depending on affinities of the SAMs. This might be in essence why the substrate-surface modification with the SAMs has a potential to affect the net functions of the PDLC films. It is of particular significance for future practical applications that electrooptic functions of PDLC films can be operated by the SAM modification of ITO-electrode surfaces. On the basis of the present findings, work is now in progress to *tune* the electrooptic functions as well as the LC aggregation features of PDLC films using SAM techniques.

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Supporting Information Available: Experimental details of the syntheses of the SAM-forming compounds and the preparation of their SAMs and the SAM properties including the advancing contact angle, ellipsometric film thickness, and XPS electron-binding energy characteristics in PDF. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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