Effect of chemisorption methods on fluorescence behavior of cyanobiphenyl units attached to silica surfaces

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Abstract

Calix[4]resorcinarene bearing four cyanobiphenyl units (CB–CRA) was synthesized and adsorbed on silica surface to reveal the binding structural effect on fluorescent behavior of cyanobiphenyl (CB) moieties bound on silica surface. A plate modified with CB–CRA exhibited a markedly low fluorescent intensity and a blue shift in the air when compared with a plate CB-modified by the silylation. The results arise from a difference in the rigidity of the spacer chains. Owing to the restricted conformation of the CB attached through the rigid CRA framework, CB units are stretched out from the silica surface, whereas the CB attached by the silylation is rather closely packed and lies on a polar silica surface because of the flexibility of the spacer chain. The fluorescence intensity of the CB–CRA was partially enhanced by the contact with cyclohexane and a less polar nematic liquid crystal, suggesting specific interactions of the CB units on the surfaces with fluid molecules. The fact that excimer formation occurs hardly on a CB–CRA plate implies that CB moiety adsorbed through the CRA orients perpendicularly to the silica surface and diluted by fluid molecules at the interface. Specific interactions between the surface CB and a liquid crystal were monitored also by changes of alignment of the liquid crystal after cell assembly; homeotropic alignment was generated immediately on a CB–CRA plate, whereas incomplete homeotropic alignment was observed on a plate modified by the CB-silylation even after a few hours. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Interfacial phenomena are closely connected with versatile functionalities of materials. One of the typical example is the alignment control of liquid crystals (LCs). It has been known that orientations of LC molecules are accurately controlled by photoinduced alterations of chemical properties as well as orientational structures of molecules tethered to substrate surfaces. For instance, azobenzene moieties attached to a surface of a silica plate trigger the orientation of a nematic LCs as a consequence, which is occurred by the strong interaction between the surface azobenzene and LC molecules [1–5]. It is based on not only of chemical structures, but also of orientation of axis of surface molecules [6]. Consequently, the effect of how to attach the surface molecules is an interesting subject in order to optimize this technique for practical applications. In our previous work [7], cyanobiphenyl (CB) residues as a fluorescent probe for revealing interfacial interactions between surface molecules

and LC molecules were tethered to a silica surface through silylation to assemble a surface model. But the work was done without any consideration of conformational effects on the interactions at a boundary region. Because CB units were introduced to a silica surface through a flexible long alkyl chain through silylation, the orientation of the CB is not controllable and randomly distributed. In order to present an approach to construct a model system to elucidate effects of the ways to link molecules on substrate surfaces [8–12], crown isomer of calix[4]resorcinarene (CRA) derivatives substituted with CB units are employed in this report for the surface modification of a substrate surface with the fluorescent probe.

The crown isomer of CRA, which has eight polar groups at the upper rim and hydrophobic tails at the lower one [13,14], is the most thermodynamically stable isomer over other isomers [15–17]. It has been shown that immersion of a fused silica plate in dilute solutions of CRA derivatives results in effective adsorption of the cyclic molecules to form self-assembled molecular films (SAMs) with high packing density owing to the multi-point adsorptivity through hydrogen bonds between polar arrays of CRA and residual silanols on a silica surface. It has also been suggested that hydrophobic tails of CRA be stretched out perpendicularly

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with respect to a substrate surface because of the rigidity of the CRA framework [13,16].

In this context, the purpose of this report is to make it clear that the restricted orientation of the fluorescent probe attached through CRA unit contribute to the intermolecular interactions between the surface CB and fluid as well as LC molecules. The results will be discussed also based on the comparison of those for chemisorbed CB through silylation, noting to differences in the flexibility of spacers. Since it has been revealed that CRA possessing eight carboxymethylated groups adsorbs firmly on a fused silica surface through hydrogen bonds [18], octacarboxymethylated CRA (CRA–COOH) bearing CB units is used in this report. Another CB compound to combine a silica surface by silylation through an alkyl chain, whose length was the same as that between CB and CRA framework of CB–CRA–COOH above mentioned, was also prepared to investigate the effect of linkage methods between CB and silica surface.

2. Experimental

Cyclohexane was of a spectroscopy grade purchased from Tokyo Kasei and used as received. Nematic LC used ($TNI = 26.6\,^{\circ}$C) is shown in Scheme 1.

CB–CRA–COOH was synthesized by hydrolysis of its octaethyl ester, CB–CRA–COOEt. These structures are shown in Scheme 2. 3-(4′-Cyanobiphenyloxy-4)propyldimethylethoxysilane (CB-SiMe$_2$OEt) was also prepared for comparison of binding structure to silica surface. Monomer model (MM) and dimer model (DM) compounds were also synthesized to show CRA structure in solution by spectral comparison. These compounds are also shown in Scheme 2.

CB–CRA–COOEt: 4-Cyano-4′-hydroxybiphenyl (49 mg, 2.5×10^{-5} mol) and K$_2$CO$_3$ (43 mg, 3.1×10^{-5} mol) were added to a DMF solution of 2,8,14,20-tetra(3-iodopropyl)-4,6,10,12,16,18,22,24-octa(ethoxycarbonyloxymethoxy)-calix[4]resorcinarene [12] (100 mg, 5.4×10^{-5} mol/2 ml). The mixture was stirred overnight at room temperature, followed by a conventional procedure. The desired compound was purified by column chromatography (SiO$_2$, ethyl acetate:hexane = 1:1) and recrystallization from 2-propanol. Yield was 72%; m.p. = 80–$81\,^{\circ}$C; ^{1}H-NMR (CDCl$_3$), δ: 1.26 (t, $J = 7$ Hz, 24H, CH$_3$), 1.7–2.3 (br, 16H, CH_2CH_2CH), 3.9–4.1 (br, 16H, OCH_2CH$_2$), 4.20 (q, $J = 7$ Hz, 16H, CH_2CH$_3$), 4.28 (s, 16H, OCH$_2$CO), 4.6–4.9 (br, 4H, CH), 6.23 (s, 4H, Ar of CRA), 6.76 (s, 4H, Ar of CRA), 6.88 (d, $J = 9$ Hz, 8H, Ar of CB), 7.39 (d, $J = 9$ Hz, 8H, Ar of CB), 7.56 ppm (s, 16H, Ar of CB).
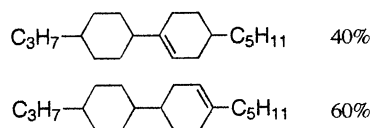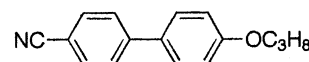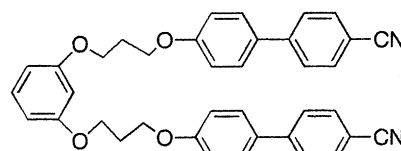

Scheme 1. The structures of used LCs.
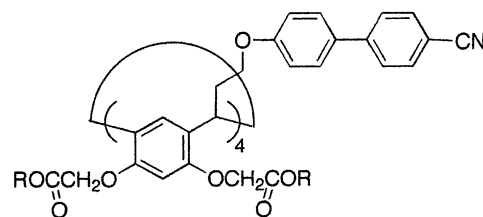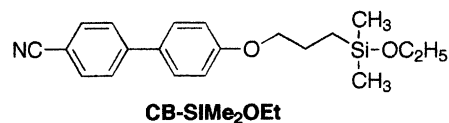
Scheme 2. Structures of used compounds.

Anal. calcd. for C$_{124}$H$_{124}$N$_4$O$_{28}$: C, 70.30%; H, 5.90%; N, 2.64%. Found: C, 70.21%; H, 5.85%; N, 2.57%.

CB–CRA–COOH: A mixture of a THF solution of CB–CRA–COOEt (40 mg, 1.0×10^{-5} mol/5 ml) and an aqueous solution of KOH (120 mg, 2.2×10^{-3} mol/5 ml) was stirred for 1 h at room temperature. After addition of ether, the aqueous phase was separated and acidified with dilute hydrochloric acid to precipitate a white solid, which was centrifuged for isolation. A THF solution of the solid was treated with charcoal to give the product (m.p. = 211–$213\,^{\circ}$C) in a 63% yield. ^{1}H-NMR (DMSO-d$_6$), δ: 1.6–1.8 (br, 8H, CH_2CH$_2$CH), 1.9–2.1 (br, 8H, CH$_2$CH_2CH), 3.9–4.1 (br, 16H, OCH_2CH$_2$), 4.28, 4.37, 4.49 and 4.58 (s each, 16H (1:2:2:1), OCH$_2$COO), 4.6–4.8 (br, 4H, CH), 6.49 (s, 4H, Ar of CRA), 6.76 (s, 4H, Ar of CRA), 6.84 (d, $J = 9$ Hz, 8H, Ar of CB), 7.46 (d, $J = 9$ Hz, 8H, Ar of CB), 7.61 (d, $J = 8$ Hz, 8H, Ar of CB), 7.74 ppm (d, $J = 8$ Hz, 8H, Ar of CB). Anal. calcd. for C$_{108}$H$_{92}$N$_4$O$_{28}$: C, 68.49%; H, 4.90%; N, 2.96%. Found C, 66.41%; H, 6.13%; N, 2.27%.

4-Cyano-4′-(2-propenyloxy)biphenyl: 3-Bromopropene (1.65 g, 13.7 mmol) and 1.40 g of K$_2$CO$_3$ (10.1 mmol) were added to a DMF solution of 4-cyano-4′-hydroxybiphenyl

(1.45 g, 7.43 mmol/100 ml), and the mixture was stirred for 2 h at 120 °C. A solid was purified by column chromatography (SiO$_2$, chloroform) and recrystallization from methanol to give the desired product (m.p. = 84.0–84.5 °C) in a 32% yield. Anal. calcd. for C$_{16}$H$_{13}$NO: C, 81.68%; H: 5.57%; N: 5.96%. Found: C, 81.59%; H, 5.41%; N, 6.12%.

CB-SiMe$_2$OEt: Dimethyl-ethoxysilane (0.21 g, 2.0 mmol) was added dropwise to a mixture of toluene solution of 4-cyano-4′-(2-propenyloxy)biphenyl (0.25 g, 1.0 mmol/2 ml) and 0.3 ml of a solution of H$_2$PtCl$_6$ in 2-propanol (0.02 mol/l). The solution was stirred for 6 h at 120 °C. CB-SiMe$_2$OEt as an oily substance was purified by column chromatography (SiO$_2$, toluene). ^{1}H-NMR (CDCl$_3$), δ: 0.12 (s, 6H, CH$_3$Si), 0.6–1.0 (m, 2H, CH$_2$Si), 1.16 (t, $J = 7$ Hz, 3H, CH$_3$), 1.6–2.1 (m, 2H, CH$_2$CH$_2$CH$_2$), 3.69 (q, $J = 7$ Hz, 2H, CH$_2$CH$_3$), 3.97 (t, 2H, OCH$_2$CH$_2$), 6.98 (d, $J = 9$ Hz, 2H, Ar), 7.52 (d, $J = 9$ Hz, 2H, Ar), 7.66 ppm (s, 4H, Ar). Anal. calcd. for C$_{20}$H$_{25}$NO$_2$Si: C, 70.76%; H, 7.42%; N, 4.12%. Found C, 71.02%; H, 7.16%; N, 4.38%.

MM: Propyl bromide (230 mg, 1.87 mmol) and 200 mg of K$_2$CO$_3$ (1.45 mmol) was added to a solution of 4-cyano-4′-hydroxybiphenyl (150 mg, 0.77 mmol) in acetone (30 ml). After the solution was refluxed for 10 h, precipitates were removed by filtration, followed by evaporation of excess propyl bromide. MM was obtained as a white solid and recrystallized from methanol; m.p. = 74.5–75.0 °C. A yield was 52%. Anal. calcd. for C$_{16}$H$_{15}$NO: C, 80.98%; H, 6.37%; N, 5.90%. Found: C, 81.22%; H, 6.42%; N, 5.71%.

1,2-Bis(3-bromopropoxy)benzene: To an ethanolic solution of resorcinol (5.00 g, 45.5 mmol) was added 1,3-dibromopropane (75.0 g, 0.373 mol) and potassium hydroxide (8.57 g, 0.159 mol), and the mixture was refluxed for 5 h. After ethanol was evaporated, diethyl ether and water was added, and an ethereal layer was washed with water. Evaporation of the solvent and unreacted 1,3-dibromopropane gave a pale brownish oil, which was subjected to silica gel column chromatography using a mixture of ethyl acetate and hexane (1/3) as an eluent to give white crystals of 1,2-bis(3-bromopropoxy)benzene (m.p. = 63–64 °C) in a 47.3% yield after recrystallization from benzene–hexane. Anal. calcd. for C$_{12}$H$_{16}$O$_2$Br$_2$: C, 40.94%; H, 4.58%; Br, 45.39%. Found: C, 42.56%; H, 4.51%; Br, 45.59%.

DM: Dimer model compound was also synthesized by the Williamson's reaction of 0.40 g of 4-cyano-4′-hydroxybiphenyl (2.0 × 10^{-3} mol) with 0.32 g of 1,2-bis(3-bromopropoxy)benzene (9.1 × 10^{-4} mol) in the presence of 0.23 g of K$_2$CO$_3$ (1.7 × 10^{-3} mol) in 50 ml of 2-butanal under reflux for 6 h. The compound was purified by column chromatography (SiO$_2$, ethyl acetate:hexane = 1:3) and recrystallization from benzene–hexane; m.p. = 143.2–144.0 °C; yield was 51%. Anal. calcd. for C$_{38}$H$_{32}$N$_2$O$_4$: C, 78.60%; H, 5.55%; N, 4.82%. Found: C, 78.32%; H, 5.41%; N, 4.97%.

Fused silica plates (9 mm × 30 mm × 1 mm) were washed in acetone, a sodium hydroxide aqueous solution, nitric acid and sodium hydrogencarbonate aqueous solution ultrasonically, followed by washing with pure water after every step. A fused silica plate was immersed in a THF solution of CB-SiMe$_2$OEt in a concentration of 5 × 10^{-4} mol/l and heated at 100 °C for 20 min after washing with THF, which was called as a CB-SiMe$_2$ plate. The preparation of a plate surface-modified with CB–CRA–COOH (CB–CRA plate) was performed by immersion of a silica plate in a 1 × 10^{-5} mol/l THF solution of CB–CRA–COOH, followed by washing with acetone ultrasonically.

Partial desorption of CB–CRA–COOH was brought by the following method. A silica plate modified with CB–CRA–COOH from CB–CRA plate according to the above-mentioned procedure was subjected to ultrasonical treatment in methanol for 10 min, followed by washing with acetone.

Assembly of LC cells were made with a drop of an LC put on a CB-modified plate, which was covered with a silica plate modified with lecithin, to fabricate a cell fixed with clips.

Absorption and fluorescence spectra were taken on a Hitachi UV320 spectrometer and an F4000 fluorospectrometer, respectively. The excitation wavelength of fluorescence spectra was 300 nm.

3. Results and discussion

3.1. Fluorescence of CB derivatives in solutions

Fluorescence spectra of the model compounds (MM and DM) and CB–CRA–COOEt were taken in cyclohexane and THF are shown in Figs. 1 and 2. The concentrations were low enough to eliminate the possibility to form intermolecular
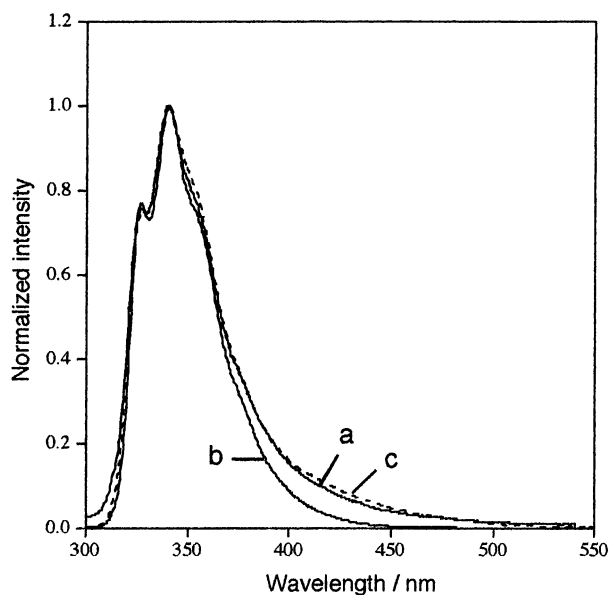

Fig. 1. Fluorescent spectra of: (a) CB–CRA–COOEt (solid line); (b) MM; (c) DM (broken line) in cyclohexane solutions.
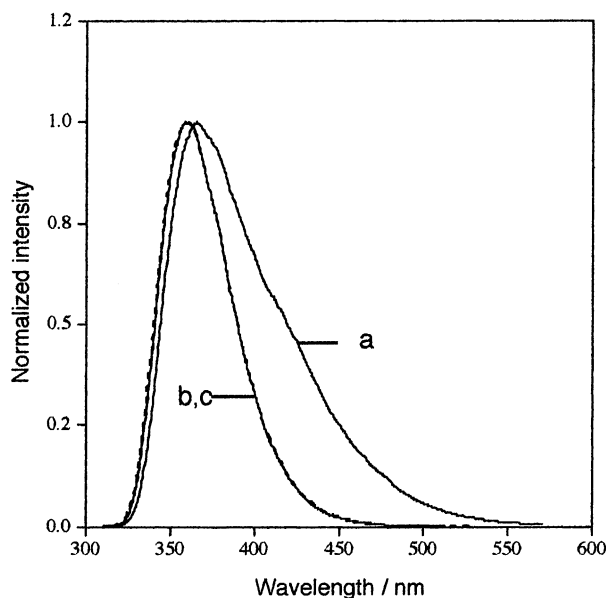
Fig. 2. Fluorescent spectra of: (a) CB–CRA–COOEt; (b) MM (solid line); (c) DM (broken line) in THF solutions.

Fig. 3. Fluorescent spectra of CB–CRA plate (solid line) and CB-SiMe$_2$ plate (dotted line) in air atmosphere.

excimer. DM displayed excimer fluorescence in less polar cyclohexane, whereas a fluorescence spectrum was almost identical with that of MM in more polar THF. These facts mean that it is profitable for two CBs linked to DM to be close in cyclohexane and far apart in THF in which DM was well solvated. In other words, solvation of THF results in the separation of the two fluorophores to hinder intramolecular excimer formation. On the other hand, CB–CRA–COOEt showed an emission band at a longer wavelength region in both solvents. The fluorescence of CB–CRA–COOEt in cyclohexane was almost the same as that of DM, which shows intramolecular excimer emission. A tail was observed at a longer wavelength region even in THF of CB–CRA–COOEt, in contrast to fluorescence of CB–CRA–COOEt and DM in THF, possessing solely monomer emission. This is because CB units of CB–CRA–COOEt are positioned close to each other even in a polar solvent, reflecting the restricted conformation.

3.2. Fluorescence of CB moieties on a silica surface

The surface modification of a silica plate with CB–CRA–COOH was conveniently carried out by dipping a silica plate in a dilute solution of CB–CRA–COOH through multi-site hydrogen bonds between COOH groups of the macrocyclic amphiphile and surface silanols of silica [12,18]. The surface density of CB on the plate was estimated to be 1.8 units/nm^2 spectroscopically. Because the molecule has four CB units, this density corresponds to an occupied area of 2.2 nm^2/molecule for a CB-modified CRA–COOEt molecule. This value is in line with the other CRA–COOEt derivatives [12,15], supporting that the molecular packing is determined specifically by the base areas of CRA–COOEt
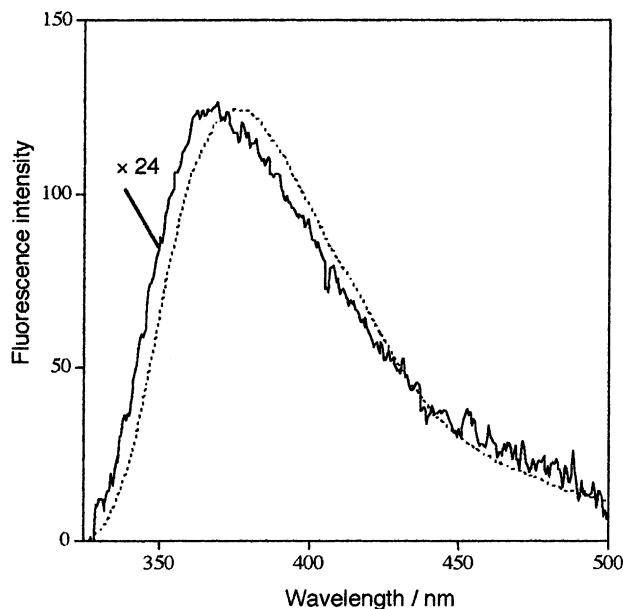
framework. The plate thus prepared is abbreviated as a CB–CRA plate.

CB-SiMe$_2$OEt was chemisorbed on a fused silica plate through O–Si–O bonds according to the conventional procedure [7]. The density of CB was 1.9 molecules/nm^2. Note that this value is not far from the density of residual silanols on a silica surface, suggesting efficient coverage of a silica surface by the silylation [19,20]. The plate treated with CB-SiMe$_2$OEt is abbreviated as CB-SiMe$_2$ plate for further discussion.

Fluorescence spectra of both modified silica plates are shown in Fig. 3. It is of noteworthy that the fluorescent intensity of CB–CRA plate is extremely weaker when compared with CB-SiMe$_2$ plate; the former was one-twenty fourth (1/24) of the latter in the intensity, whereas adsorbed amounts of CB units were similar. It is hard to explain such marked fluorescence quenching for the CB–CRA plate, but it is probably caused by orientated CB being packed so densely on the plate. In order to check this assumption, the loading of the CB on a CB–CRA plate was reduced by treatment with methanol to cause partial desorption of CB–CRA–COOH. A UV absorption spectrum shown in Fig. 4 indicates that an amount of CB adsorbed on the plate is reduced approximately by a half. λ_{max} of the plate treated with methanol suffers from a slight red-shift, suggesting the reduction of interactions between the CB units in the ground state. On the other hand, the fluorescent intensity of the plate of the low loading of CB was almost twice that of the CB–CRA plate before washing with methanol, whereas a shoulder at a long wavelength region disappears for the plate with the low CB loading. These results are in line with the above-mentioned assumption that the fluorescence quenching for the CB–CRA
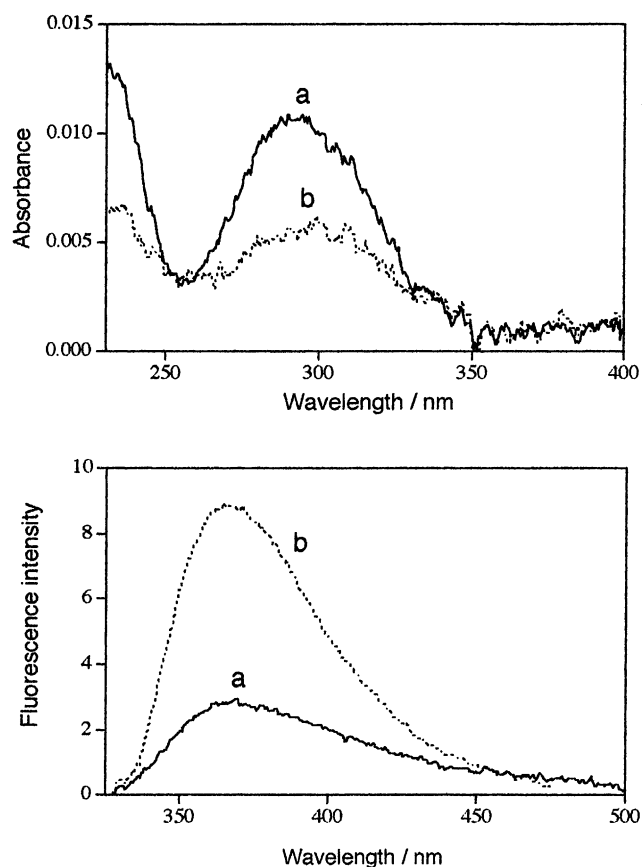
Fig. 4. Absorption and fluorescent spectra of thinned CB–CRA plate (b) (dotted line) compared with original CB–CRA plate (a) (solid line) in air atmosphere.

Fig. 5. Fluorescent spectra of CB–CRA plate (solid line) and CB-SiMe$_2$ plate (dotted line) immersed in cyclohexane.

plate comes from the high density of CB units on a surface. There is no information that shows what occurs in high density of CB, but there is a possibility that orientated CB caused energy migration followed by non-radiative deactivation to silica surface or framework structure of CRA efficiently.

The fluorescent maximum appears at 367 nm for the CB–CRA plate, while the CB-SiMe$_2$ plate has the maximum at 378 nm, suggesting that micropolarity around the
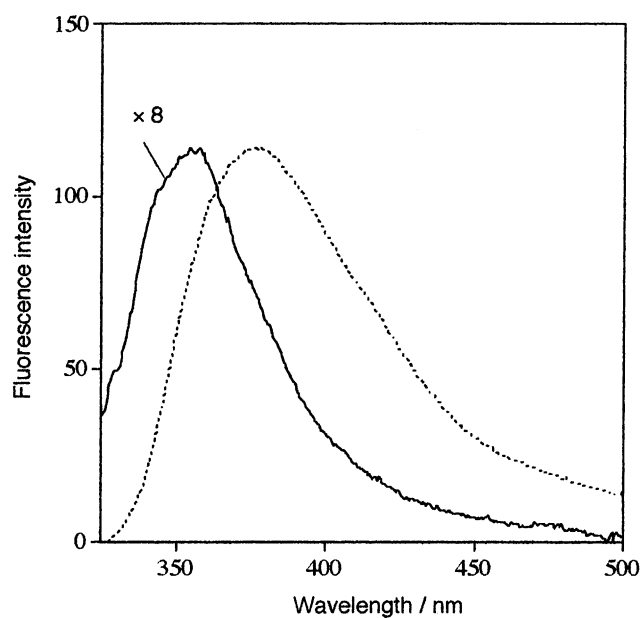
CB on the former plate is higher than that of the latter, as discussed in a previous work that examined CB fluorescent spectra in solutions of various polarity [7]. This situation implies that the CB of the CB-SiMe$_2$ plate lies much closer to a polar silica surface of fused silica probably because of the flexible spacer chain. There is a slight difference in the spectral shape between the two plates. A shoulder exists at long wavelength region for CB–CRA plate, suggesting the partial formation of excimer.

Based on these, illustrations of the surface CB units are shown in Scheme 3. The CB units of a CB–CRA plate with a dense packing of the CRA base framework is forced to be stretched out from a surface owing to the rigidity of the cyclic framework so that intimate molecular interactions among CB moieties are generated. On the other hand, CB units on a CB-SiMe$_2$ plate lie on a polar silica surface.
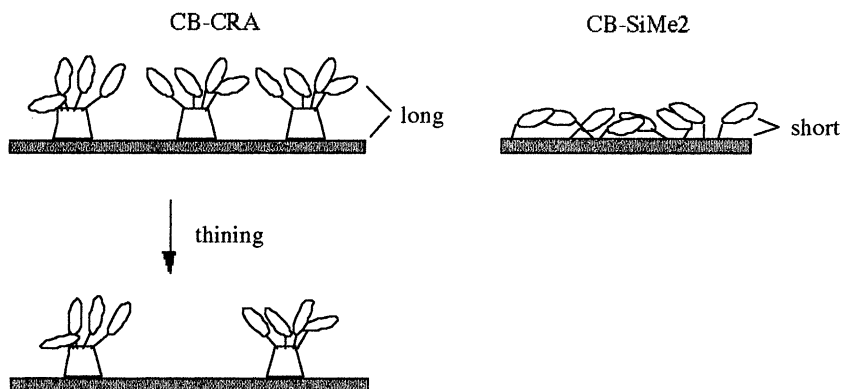
Scheme 3. Illustrations of CB moieties at the surface of CB–CRA plates and a CB-SiMe$_2$ plate.
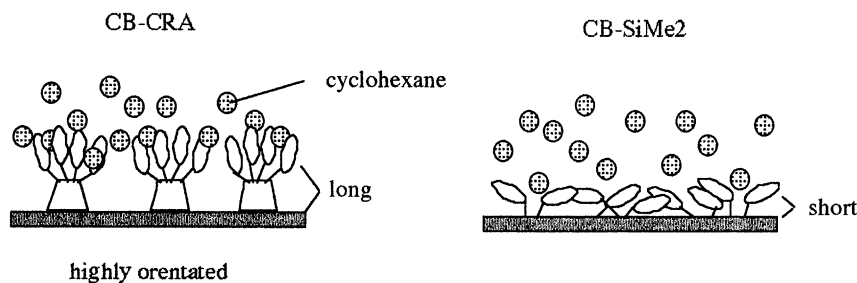
Scheme 4. Illustrations of CB moieties at the interface of a CB–CRA plate and a CB-SiMe$_2$ plate exposed to cyclohexane.

3.3. Fluorescence of CB-modified silica plates exposed to cyclohexane

Fig. 5 shows fluorescence spectra of both the plates immersed in cyclohexane. Whereas the emission intensity of a CB–CRA plate is still weaker than that of a CB-SiMe$_2$ plate, relative intensity of the former is partially recovered. The intensity is three times larger when compared with the fluorescence measured in the air. The fluorescent maximum was blue shifted to 355 nm, while a shoulder in a long wavelength region disappears as a result of the exposure to the solvent, implying a significant role of cyclohexane molecules as a diluent. Consequently, the enhancement of fluorescence induced by the exposure to cyclohexane is originated from the suppression of direct molecular interactions between CB units due to the dilution effect of solvent molecules. This is similar to the dilution by washing in methanol mentioned above. The blue shift and disappearance of shoulder imply that the polarity around CB units become lower and the relative position of CB each other
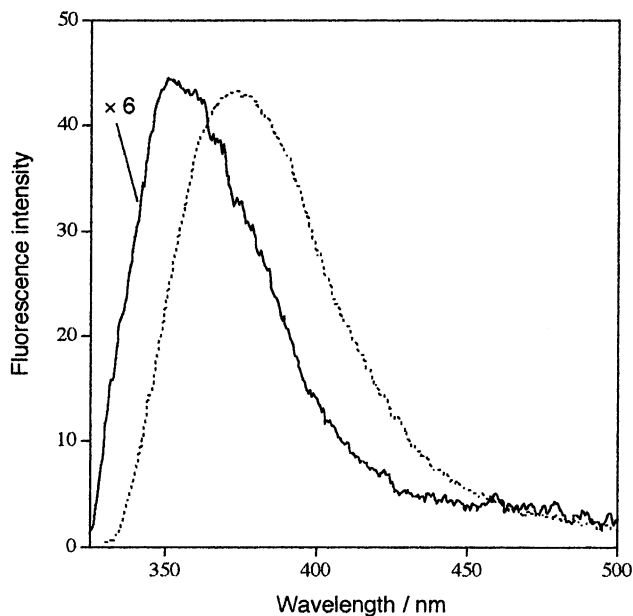
hinder CB excimer from forming. In the case of a CB-SiMe$_2$ plate, no orientational alteration of CB is induced even upon exposure to cyclohexane, probably because its interactions with less polar solvent is suppressed owing to relatively high polarity of CB unit. CB units exposed to cyclohexane are illustrated in Scheme 4.

3.4. Fluorescence of CB-modified silica plates in contact with an LC

Fluorescence spectra of CB-modified plates were taken after wetting with a nematic LC with polarity similar to that of cyclohexane. As shown in Fig. 6, the fluorescent
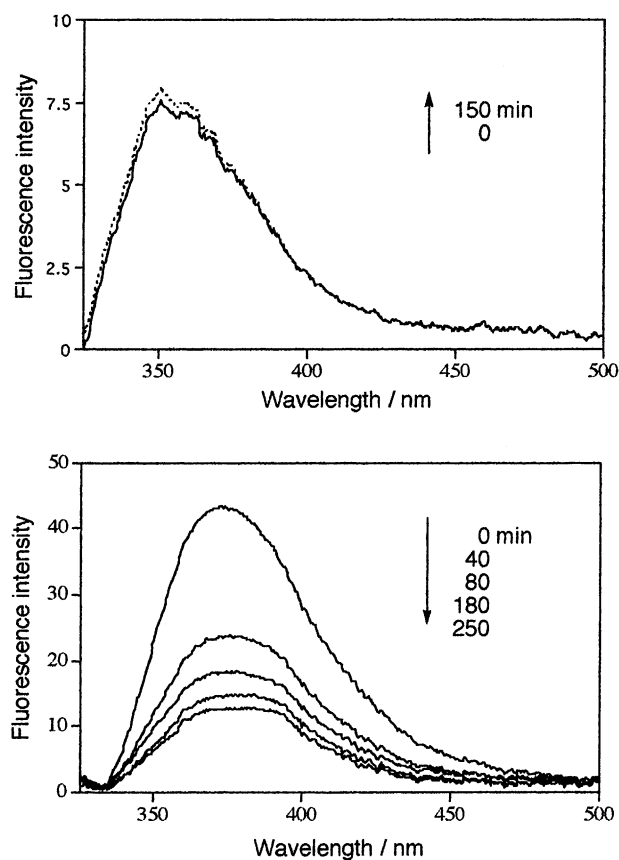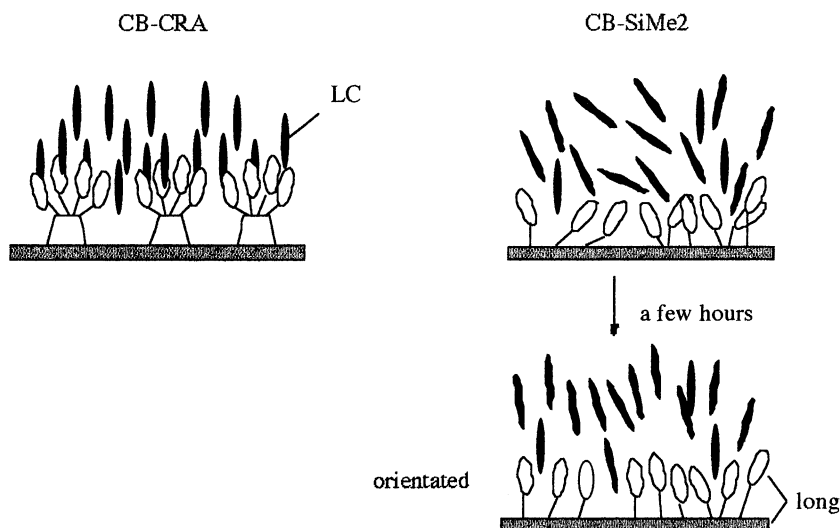

Fig. 6. Fluorescent spectra of CB–CRA plate (solid line) and CB-SiMe$_2$ plate (dotted line) immersed in the LC.

Fig. 7. Time dependence of fluorescent spectra of CB–CRA plate (upper) and CB-SiMe$_2$ plate (lower) after immersing in the LC.

CB-CRA   CB-SiMe2

Scheme 5. Illustrations of CB moieties at the interface of a CB–CRA plate and a CB-SiMe$_2$ plate exposed to LC.

intensity of CB-SiMe$_2$ plate was one-sixth (1/6) compared with CB–CRA plate in LC. The spectral shape of CB–CRA plate was essentially the same as that taken in cyclohexane, suggesting that molecular interaction between LC molecules and CB units on CB–CRA plate is similar to those between cyclohexane and CB. In contrast to the CB–CRA plate, a CB-SiMe$_2$ plate wetted with the LC displayed a blue shift of the fluorescence maximum from 378 to 372 nm, while a shoulder at a long wavelength region decreased. As mentioned just above, cyclohexane exhibits no role in fluorescence behavior of the CB on the CB-SiMe$_2$ plate. In contrast, LC molecules show the significant effect on the fluorescent behavior, indicating a specific interaction of the mesogenic molecules with mesogenic CB units even on the CB-SiMe$_2$. Fluorescence spectra shown in Fig. 6 indicate also that the micro-environmental polarity around the CB units on a CB–CRA plate is still much lower than that on CB-SiMe$_2$ plate. The interplay among the CB units on the CB–CRA is still remarkable owing dense packing compared with the CB-SiMe$_2$ plate.

Fig. 7 shows fluorescence spectra of both CB-modified plates as a function of time after the contact with the liquid. The fluorescent intensity of the CB on a CB-SiMe$_2$ plate decreased gradually and markedly, whereas no change was observed for a CB–CRA. These results show that specific interactions of the CB residues with LC molecules occurs very slowly on the CB-SiMe$_2$ plate, while intermolecular interactions for the CB–CRA/LC system are complete before the measurement. The intermolecular interactions of the CB with LC molecules on the former plate result in the conformational rearrangement of the fluorescent moieties to make high orientation and high density of CB units that cause fluorescent quenching. This kind of contrasting behavior between the two CB-modified plates reflects evidently the difference in the level of conformational restriction by the spacers linking the CB on a silica surface.

In order to obtain further information about the effect of chemisorption methods on interactions of the CB with LCs, LC cells were assembled by sandwiching the nematics between a CB-modified plate and a lecithin-treated silica plate. The modification with lecithin gives rise homeotropic (perpendicular) alignment of LCs so that LC alignment in the hybrid cells is determined solely by the CB-modified plate. When a CB–CRA plate was used, a random parallel texture just after the cell assembly was transformed into homeotropic alignment. A CB-SiMe$_2$ plate resulted also in random parallel alignment after the cell assembly. The alignment was changed only partially into homeotropic one even after the storage for a month at room temperature. The results disclose clear-cut dependence of LC alignment on the nature of spacers.

The orientational transformation of CB residues induced by wetting with a nematic LC is illustrated in Scheme 5. The CB on a CB-SiMe$_2$ is densely packed in a molecular layer, while a free space is ensured for CB units on a CB–CRA plate, which is made by firm structure of CRA framework. The penetration of LC molecules into a CB–CRA layer occurs more efficiently when compared with a CB-SiMe$_2$ molecular layer.

4. Conclusions

Comparative studies on fluorescence behavior of CB units were performed by the preparation of molecular films through the surface adsorption of a CRA derivative to give a CB–CRA plate and the silylation of a CB derivative to prepare a CB-SiMe$_2$ to extract effects of the linkage of the fluorescent probe to a silica surface. A calix[4]resorcinarene with four CB units at the lower rim (CB–CRA) showed excimer emission at long wavelength not only in a less polar solvent, but also in a polar solvent, meaning that the CB

units are faced closely to each other because of the rigidity of the macrocyclic framework. The CB–CRA substituted with eight COOH groups at the upper rim forms densely packed SAM on a silica plate from its dilute THF solution owing to multi-site adsorptivity. The self-assembled CB units introduced to a silica surface using CB–CRA exhibits a marked self-quenching of fluorescence owing to the dense packing leading to non-radiative deactivation, compared with the emission of the CB tethered to a silica surface through the silylation.

When a CB–CRA plate is immersed in cyclohexane, fluorescence of the CB is partially recovered, whereas no change in both fluorescence intensity and spectral shape is induced for a CB upon even exposure to the solvent. The difference in such emission behavior between the two kinds of plates is ascribable to difference in compatibility of molecular films with cyclohexane. A CB layer derived from CB–CRA possesses a free space since the packing density is specifically determined by the CRA moiety so that the reorientation of CB moieties is caused as a result of a dilution effect of the solvent. On the other hand, a CB molecular film chemisorbed on a CB-SiMe$_2$ is so densely packed that relatively polar CB residues exhibit less compatibility with less polar cyclohexane.

The level of molecular interactions of the CB with a less polar LC is also influenced crucially by the surface modification. The wetting of a CB plate with the LC induces gradual decrease in fluorescence intensity of the CB, while no modification is observed for a CB–CRA plate. This kind of different behavior of the fluorescent probe suggests also that intimate interactions are affected by the attachment of the CB units. This situation was confirmed by the observation that a CB–CRA plate brings about homeotropic alignment of the LC, whereas homeotropic alignment occurs insufficiently for a CB-SiMe$_2$ plate.

In conclusion, fluorescence measurements of CB as an emission probe provide vivid information concerning intra- and intermolecular interactions at interfacial regions.

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