JOURNAL OF
Materials
CHEMISTRY

Enhancement of desorption resistance of adsorbed monolayers of calix[4]resorcinarenes bearing cinnamoyl residues by photodimerization

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Received 2nd January 2001, Accepted 31st March 2001
First published as an Advance Article on the web 14th May 2001

The crown conformer of a calix[4]resorcinarene (CRA) possessing eight carboxymethylated units at the lower rim and four cinnamoyl residues at the upper rim was prepared to fabricate photofunctional monomolecular layers. The CRA derivative was adsorbed on a fused silica plate from a THF solution to form a monomolecular layer through hydrogen bonds. The monolayer exhibited photocycloaddition, together with photoisomerization, upon UV irradiation. Whereas the desorption of the macrocyclic compound from the plate occurred partially in polar solvents including ethanol, UV irradiation exhibited a suppressive effect on the desorption, suggesting that the number of hydrogen bonds between the molecules and a silica surface per molecule are much enhanced by intermolecular photodimerization of the cinnamoyl residues leading to an increment of the molecular weight of the adsorbate. The monolayer of the CRA on a silica plate exhibited the ability to transform the alignment of a nematic liquid crystal upon UV irradiation from homeotropic (perpendicular) to planar (parallel) orientation. The photoalignment of the liquid crystal was stabilized toward heat treatment possibly owing to the photodimerization of cinnamoyl units.

Introduction

Calix[4]resorcinarenes (CRAs) have been attracting current interest from a viewpoint of host guest chemistry to achieve molecular recognition.[1–3] From a synthetic point of view, the crown conformer is also attractive because it is the most thermodynamically stable isomer among the others including partial cone, alternate and 1,3-partial alternate, leading to good availability.[4,5] Our major concern with the crown isomer of CRAs and their derivatives has been concentrated on their surface adsorption behavior to assemble functional monolayers on solid surfaces. We have reported that crown conformers of CRAs and O-carboxylated and O-hydroxyethylated derivatives adsorb readily on polar surfaces such as a silica surface from dilute solutions of less polar solvents to form self-assembled monolayers (SAMs) with relatively dense packing.[6–9] The efficient adsorptivity of the macrocyclic amphiphiles on polar substrates such as silica plates and poly(vinyl alcohol) films originates from multi-site interactions between the polar heads and the polar surfaces to form hydrogen bonds effectively. This procedure provides a very convenient way to fabricate SAMs bearing versatile functional residues, which are introduced readily to the other rim of the cyclic framework.[10] It is worthy of mention that photoisomerization of azobenzene introduced to the hydrophobic tails of CRA occurs efficiently even in a densely packed self-assembled monolayer of the corresponding CRA, whereas the *E*-to-*Z* photoisomerization requires a free space because drastic molecular shape change is involved.[11] This is because the molecular packing density of the CRA is specifically determined by the base area of the macrocycles so that sufficient free space is ensured for the azobenzene layer since the cross-section of four (*E*)-azobenzene residues is smaller than the base area of the CRA. This situation enabled us to achieve the reversible photocontrol of dispensability of colloidal silica particles, the surface of which is modified by a CRA substituted with four azobenzenes, when the photoresponsive tiny particles are suspended in less polar solvents.[8] Because the monolayer formation of CRA and its derivatives arises from hydrogen bonds between the macrocyclic molecules and polar solid surfaces, desorption is not suppressed when substrate plates covered with the CRA monolayers are immersed in polar solvents such as alcohols and water. In this context, the improvement of desorption resistance even in polar solvents has been required in order to make the present procedure for SAM fabrication more attractive. We have reported recently that the desorption resistance of CRA derivatives with eight O-carboxylmethylated residues (CRA-CM) is markedly enhanced by the modification of a silica surface with an aminoalkyl silylating reagent to lead to the surface adsorption through interactions between NH_2 and COOH groups.[12]

We report here an alternative method to enhance the desorption resistance by intermolecular photocycloaddition of a CRA-CM derivative bearing cinnamate residues. The idea is based on the fact that an increment of adsorption sites of adsorbates leads to an increase in the adsorption strength,[13] as exemplified by the sticking of a barnacle through the enzymatic crosslinking of an adhesive protein.[14] The purpose of this report is two-fold. First, a CRA derivative with cinnamoyl residues is prepared to assemble a surface-adsorbed monolayer to show that the desorption even in alcoholic solvents is in fact suppressed by the photocycloaddition of cinnamoyl residues tethered to the upper rim of the cyclic framework. Second, a monolayer of the CRA with cinnamoyl residues on a silica plate is applied to perform the photocontrol of liquid crystal alignment in order to display the photofunctionality of the monolayer.

Experimental

Materials

(*E*)-*N*,*N*-Diethyl-4-hydroxycinnamamide. 4-Acetoxycinnamic acid (1.59 g, 7.70 mmol) was treated with 2 ml of thionyl chloride

DOI: 10.1039/b100034i

in 4 ml of benzene to give the corresponding acid chloride, which was reacted with diethylamine (1.73 g, 2.37 mmol) in benzene to produce *N*,*N*-diethyl-4-acetyloxycinnamamide. The product was purified by column chromatography on silica gel using ethyl acetate as an eluent to give a pale brown oil in a 48.6% yield. An NMR spectrum supported the *E*-configuration.

^{1}H-NMR($CDCl_3$) δ (ppm) = 1.18 (q, 6H, CH_3), 2.28 (s, 3H, CH_3CO), 3.45 (q, 4H, NCH_2), 6.75 (d, 1H, $J = 15$ Hz, COCH=),7.07 (d, 2H, $J = 7$ Hz, Ar-H), 7.51 (d, 2H, $J = 7$ Hz, Ar-H), 7.67 (d, 1H, $J = 15$ Hz, ArCH=). Anal. Calcd. for $C_{15}H_{19}NO_3$, C: 68.95, H: 7.33, N: 5.36%. Found, C: 68.87, H: 7.35, N: 5.19%.

The cinnamamide thus prepared (0.97 g, 3.7 mmol) dissolved in methanol was treated with potassium hydroxide (1.57 g, 0.028 mol) for 30 minutes at room temperature, followed by acidification with hydrochloric acid. After removal of the solvent, the product was extracted with ethyl acetate to give yellowish white crystals which were purified by recrystallization with a mixture of ethyl acetate and hexane. Yield was 54%.

^{1}H-NMR($CDCl_3$) δ (ppm) = 1.21 (q, 6H, CH_3), 3.47 (q, 4H, NCH_2), 6.65 (d, 1H, $J = 15$ Hz, COCH=), 6.87 (d, 2H, $J = 7$ Hz, Ar-H), 7.38 (m, 3H, Ar-H + OH), 7.64 (d, 1H, $J = 15$ Hz, ArCH=). Anal. Calcd. for $C_{13}H_{17}NO_2$, C: 71.21, H: 7.81, N: 6.38%. Found, C: 71.10, H: 7.75, N: 6.27%.

2,8,14,20-Tetrakis{3-[4-(2-diethylaminocarbonylethenyl)phenoxy] propyl}-4,6,10,12,16,18,22,24-octakis(carboxymethoxy)calix[4]-arene (1). The calix[4]resorcinarene possessing four iodopropyl residues (**3**) was prepared according to the previous paper.[9] To a solution of **3** (0.41 g, 0.22 mmol) in 15 ml of THF was added *N*,*N*-diethyl-4-hydroxycinnamamide (0.27 g, 1.2 mmol) and potassium carbonate (0.18 g, 1.3 mmol). The mixture was stirred for 24 h at room temperature. After the solvent was evaporated, a residue was diluted with ethyl acetate and washed with water. An organic layer was condensed to give a crude CRA with four cinnamoyl residues (**2**) as a brown sticky oil in a 71% yield.

^{1}H-NMR($CDCl_3$) δ (ppm) = 1.28 (m, 48H, CH_3), 1.98–2.19 (m, 32H, $C\underline{H_2}C\underline{H_2}CH$), 3.47 (m, 16H, NCH_2), 3.99 (t, 32H, $ArOCH_2$), 4.25 (m, 32H, $OCH_2CO + COOCH_2$), 4.73 (t, 4H, CH), 6.23 (s, 4H, Ar-H), 6.63 (d, 4H, $J = 16$ Hz, COCH=), 6.72 (s, 4H, Ar-H), 6.79 (d, 8H, $J = 8$ Hz, Ar-H), 7.36 (d, 8H, $J = 8$ Hz, Ar-H), 7.62 (d, 4H, $J = 16$ Hz, Ar-CH=). Anal. Calcd. for $C_{124}H_{156}N_4O_{32}$, C: 67.25, H: 7.10, N: 2.53%. Found, C: 66.97, H: 7.16, N: 2.31%.

A potassium hydroxide aqueous solution (0.45 g in 20 ml water) was added to a solution of **2** (0.46 g, 0.21 mmol) in 50 ml THF, and the mixture was stirred for 1 h at room temperature, followed by acidification with hydrochloric acid to give a white precipitate of mp = 153–155 °C in 56% yield.

^{1}H-NMR(DMSO-d_6) δ (ppm) = 1.09 (m, 24H, CH_3), 1.69–1.9 (m, 16H, $C\underline{H_2}C\underline{H_2}CH$), 3.47 (m, 16H, NCH_2), 3.95 (t, 32H, $ArOCH_2$), 4.20–4.48 (q, 32H, OCH_2CO), 4.63 (t, 4H, CH), 6.43 (s, 4H, Ar-H), 6.70 (s, 4H, Ar-H), 6.80 (d, 8H, $J = 8$ Hz, Ar-H), 6.87 (d, 4H, $J = 16$ Hz, COCH=), 7.38 (d, 4H, $J = 16$ Hz, Ar-CH=), 7.51 (d, 8H, $J = 8$ Hz, Ar-H). Anal. Calcd. for $C_{108}H_{124}N_4O_{32}$, C: 65.18, H: 6.28, N: 2.81%. Found, C: 64.89, H: 6.46, N: 2.65%.

***N*,*N*-Diethyl-4-propoxycinnamamide (4).** A mixture of 1-bromopropane (4.01g, 30.0 mmol), potassium carbonate (4.14 g, 0.0300 mol), *N*,*N*-diethyl-4-hydroxycinnamamide (4.38 g, 20.0 mmol) and sodium iodide (2.0 g, 1.3 mmol) in 50 ml of acetone was refluxed for 8 h, followed by evaporation of the solvent. The residue was dissolved in ethyl ether, and the organic layer was washed with water and evaporated to yield a pale brownish oil.

^{1}H-NMR($CDCl_3$) δ (ppm) = 1.03 (t, 3H, $C\underline{H_3}CH_2CH_2$), 1.21 (m, 6H, $C\underline{H_3}CH_2N$), 1.80 (m, 2H, $CH_3C\underline{H_2}CH_2$), 3.48 (m, 4H, NCH_2), 3.92 (t, 2H, OCH_2), 6.70 (d, 1H, $J = 16$ Hz, COCH=), 6.87 (d, 2H, $J = 7$ Hz, Ar-H), 7.45 (m, 3H, Ar-H + OH), 7.67 (d, 1H, $J = 15$ Hz, ArCH=). Anal. Calcd. for $C_{16}H_{23}NO_2$, C: 73.53, H: 8.87, N: 5.36%. Found, C: 73.36, H: 9.09, N: 5.41%.

1,3-Bis{3-[4-(2-diethylaminocarbonylethenyl)phenoxy]propoxy} benzene (5). To an ethanol solution of resorcinol (5.00 g, 0.0455 mol) 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 the ethanol was evaporated, diethyl ether and water were added, and the ethereal layer was washed with water. The evaporation of the solvent and unreacted 1,3-dibromopropane under reduced pressure gave a pale brownish oil, which was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane (1 : 3 v/v) as an eluent to give colorless crystals of 1,2-bis(3-bromopropoxy)benzene of mp = 62–64 °C in 47.3% yield after recrystallization from a mixture of benzene and hexane.

A solution of 1.00 g of 1,2-bis(3-bromopropoxy)benzene (2.84 mmol) and 2.49 g of *N*,*N*-diethyl-4-hydroxycinnamamide (1.14 mmol) in 50 ml of THF was refluxed for 10 h in the presence of 1.58 g of potassium carbonate (1.14 mmol) and 1.71 g of sodium iodide (1.14 mmol). The reaction mixture was diluted with ethyl acetate and washed with water. The evaporation of the solvent was followed by silica gel column chromatography using a 6 : 1 (v/v) mixture of ethyl acetate and hexane as an eluent to give crystals of mp = 116–117 °C in 28% yield after recrystallization from a mixture of benzene and hexane.

^{1}H-NMR($CDCl_3$) δ (ppm) = 1.14 (m, 12H, CH_3), 2.19 (m, 4H, $CH_2C\underline{H_2}CH_2$), 3.40 (q, 8H, NCH_2), 4.09 (m, 8H, OCH_2), 6.40–6.50 (m, 3H, Ar-H), 6.62 (d, 2H, $J = 15$ Hz, COCH=), 6.83 (d, 4H, $J = 9$ Hz, Ar-H), 7.00–7.30 (m, 1H, Ar-H), 7.40 (d, 4H, $J = 9$ Hz, Ar-H), 7.60 (d, 2H, $J = 15$ Hz, ArCH=). Anal. Calcd. for $C_{38}H_{48}N_2O_6$, C: 72.59, H: 7.69, N: 4.45%. Found, C: 72.36, H: 7.66, N: 4.36%.

Adsorption experiments for 1

Fused silica plates were washed ultrasonically in a series of solvents in the following order; acetone, water, aqueous KOH solution, water, nitric acid, water, saturated aqueous solution of $KHCO_3$ and water. A fused silica plate was immersed in a THF solution of **1** of $1–2 \times 10^{-4}$ mol dm^{-3} for 10–20 min at room temperature, followed by washing with acetone to remove a excess amount of **1**. The amount of **1** adsorbed on the plate was estimated by UV absorption spectroscopy under the assumption that no modification of absorption coefficient of the cinnamoyl residue is made by surface adsorption.

Photochemistry

A spectroirradiator equipped with a diffraction grating and a Xe-lamp, CRM-FA (JASCO), was used for photoirradiation of **1** and model compounds in acetonitrile solutions and on fused silica plates. The band width of light was ±7 nm. Acetonitrile is convenient for photoreaction study because it is transparent at >190 nm light. Solution photochemistry was followed by taking UV-visible absorption spectra on a diode array spectrometer, HP8452A (Hewlett Packerd), while UV-visible absorption spectra of surface-modified quartz plates were recorded on a HITACHI UV-320.

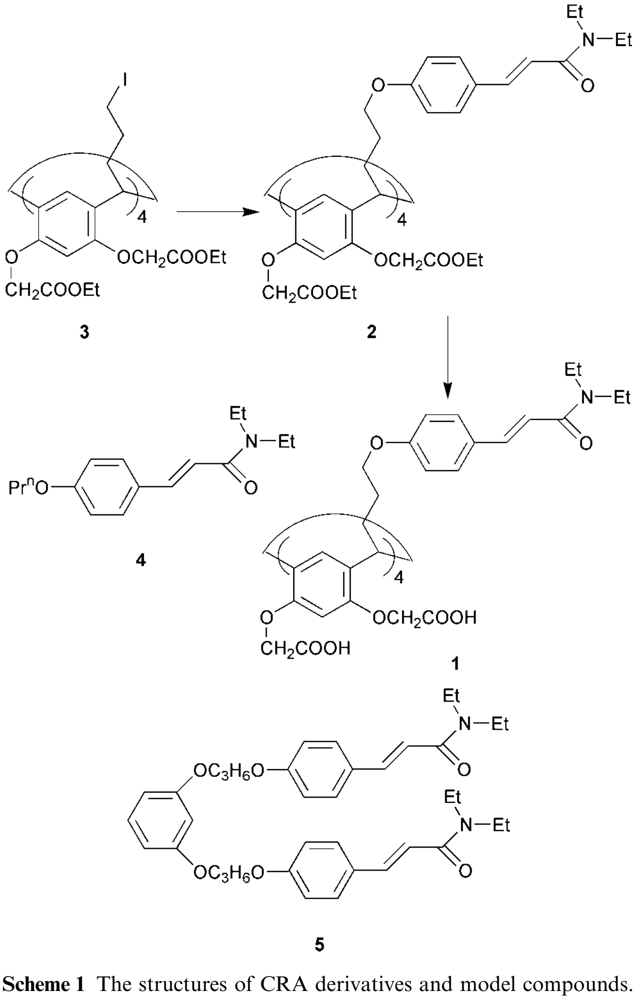
Fabrication of liquid crystal cells

A fused silica plate adsorbing **1** was exposed to light in a wavelength range from 290 to 390 nm from a super-high pressure mercury arc (USH-500D, Ushio electronics, 1.5 mW cm^{-2} at 365 nm) passed through a glass filter (UV-D35; Toshiba) and a photomask. Subsequently, a liquid crystal cell was prepared by sandwiching 4-cyano-4′-pentylbiphenyl ($T_{NI} = 35.4$ °C) as a nematic liquid crystal between the photoirradiated quartz plate and a quartz plate which was treated with lecithin for homeotropic alignment. Birefringent photoimages recorded in the cell were observed with a polarized microscope, OLYMPUS BH-2.

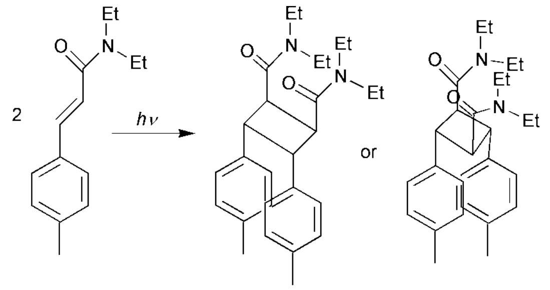
Results and discussions

Molecular design and synthesis

It is well-known that photoirradiation of cinnamic acid and its derivatives in the solid state results in (2+2) cycloaddition which provides a convenient way to link two molecules through a covalent bond. It followed that a molecular design has been made to tether cinnamoyl groups to the methylene bridges of the CRA moiety with eight carboxymethoxy groups (CRA-CM). Since alkaline hydrolysis is involved in the synthesis of CRA-CM through the corresponding octaester derivative, cinnamamide was employed here owing to its resistance to alkaline media. When compared to cinnamic acids and cinnamates, little work has been done on the photodimerzation of cinnamamides.[15,16] As described in our preceding paper, a crown conformer of a CRA substituted with four 3-iodopropyl residues at the lower rim and eight ethoxycarbonylmethoxy residues at the upper rim (**3**) is a convenient intermediate to introduce four photofunctional groups to the cyclic skeleton through the Williamson reaction.[9] In this way, **3** was treated with *N*,*N*-diethyl-4-hydroxycinnamamide to give **2** which was subjected to alkaline hydrolysis to yield the desired product (**1**) (Scheme 1). Two cinnamamide units that orientated in the same side on a plate gives also photocycloaddition products, which are shown in Scheme 2. The photoaddition can occur intermolecularly as well as intramolecularly. For the comparison with solution photochemistry, both a monomer model compound (**4**) and a dimer model compound (**5**) were also synthesized. Compound **4** has one cinnamamide unit with a propoxy group whereas **5** has two cinnamamide moieties, which are linked at the *meta*-positions of the benzene ring through five chain atoms in order to resemble the partial structure of **1**.



Scheme 1 The structures of CRA derivatives and model compounds.



Scheme 2 Photocycloaddition products of cinnamamide units.

Solution photochemistry

It is known that cinnamamide isomerizes reversibly between *E*-isomer and *Z*-isomer under photoirradiation and displays no thermal isomerization.[17] This was confirmed as shown in Fig. 1(a). UV-irradiation of an acetonitrile solution of the model compound **4** with 330 nm light, which was a longer shoulder wavelength of the *E*-isomer but was not an absorption band of the *Z*-isomer, induced spectral changes accompanied by the appearance of an isosbestic point at 274 nm and a blue shift of $\lambda_{\max}$ from 282 to 268 nm due to *E*-to-*Z* photoisomerization. Exposure of the irradiated solution to 259 nm light, which is the wavelength of largest different absorbance between the *Z*-isomer and the *E*-isomer, recovered the spectrum due to the *E*-isomer, holding the isosbestic point, as shown in

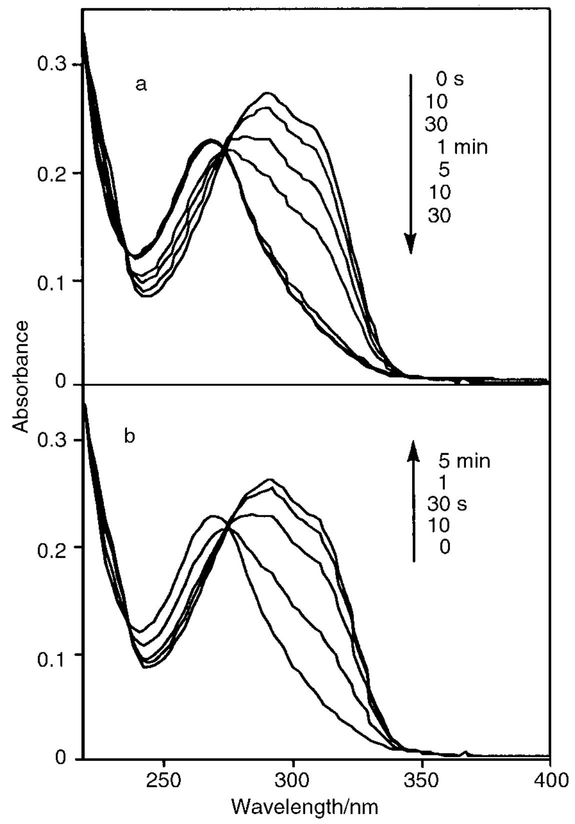


Fig. 1 UV-visible spectral changes of **4** in acetonitrile (a) under 330 nm photoirradiation and (b) under 259 nm photoirradiation after 330 nm irradiation to give a photostationary state.

Fig. 1(b). Compound **4** also showed *E*-to-*Z* photoisomerization at 300 nm, which was the λ_{max} of the *E*-isomer. An acetonitrile solution of 6×10^{-3} mol dm^{-3} of **4** was irradiated with 330 nm light for 1 h to give a photostationary state. The solvent was removed under reduced pressure, and a residual product was subjected to ^{1}H-NMR spectrum measurement to elucidate the product distribution. ^{1}H-NMR measurement revealed that the product is assigned to be the *Z*-isomer having doublet peaks of olefinic protons at 5.93 and 6.52 ppm ($J = 12$ Hz) while doublet peaks due to the *E*-isomer olefinic protons appear at 6.70 and 7.67 ppm ($J = 16$ Hz). It should be stressed that chemical shifts of the *N*-ethyl protons are quite different between the *E*- and *Z*-isomers. Broad peaks due to the methylene protons of the *E*-isomer centered at 3.5 ppm are changed into two quartets at 3.29 and 3.58 ppm for the *Z*-isomer whereas a broad peak at 1.2 ppm for six protons of the *E*-isomer is converted into two triplet peaks at 0.99 and 1.18 ppm for the *Z*-isomer. The environments of the two ethyl groups are equivalent in the *E*-isomer because of the easy rotation around the CO–N bond. On the other hand, the two ethyl groups are not equivalent to each other for the *Z*-isomer, since the rotation around the CO–N bond is suppressed because of steric hindrance. These facts imply that the *E*-isomer is s-*cis* while the *Z*-isomer is s-*trans*. A predominant product at the photostationary state under 259 nm irradiation of **4** was identified as the *E*-isomer by ^{1}H-NMR analysis.

Photochemical behavior of the dimer model (**5**) was slightly different from that of **4**. Irradiation of **5** in acetonitrile with 300 or 330 nm light brought about spectral changes quite similar to those of **4** due to exclusive *E*-to-*Z* photoisomerization to form a mixture of *E*- and *Z*-isomers. On the other hand, irradiation with 259 nm light resulted in a decrease in the absorbance at a shorter wavelength region without change in λ_{max} at 292 nm as shown in Fig. 2. We achieved ED-diagram analysis of the spectral changes to reveal whether any side reaction is involved upon 259 nm irradiation. ED-diagrams consist of plots of absorbance changes at arbitrary wavelengths toward those at a basis wavelength so that their linearity indicates the involvement of a single chemical reaction.[18] An ED-diagram for 259 nm irradiation deviated from linearity, implying the occurrence of side reaction(s). The structural elucidation of a photoproduct other than the geometrical isomers was unsuccessful because of its minute formation, while it was anticipated that intramolecular cycloadduct(s) is formed. The photoproducts of **5** after prolonged irradiation with 259 nm light in the dilute acetonitrile solution were corrected by evaporation of solvent to identify the product(s). According to ^{1}H-NMR measurements, *Z*-isomer isomerized from *E*-isomer was observed and their ratio was 15 : 85 (*Z*-isomer : *E*-isomer). Though the total peak integration of double bonds reduced by 10%, no new peak of evidence of photocycloaddition appeared. These results suggest that intramolecular photocycloaddition takes place for **5** under irradiation with 259 nm light, whereas essentially no photocycloadduct is formed under irradiation with light at the longer wavelengths.

The photochemistry of **2** in a dilute acetonitrile solution consisted solely of *E*/*Z* isomerization upon irradiation with 330 nm light, which the *Z*-isomer does not absorb, as demonstrated by the presence of an isosbestic point in the spectral changes and the linearity of their ED-diagram. On the other hand, prolonged irradiation of the solution with 300 nm light induced side reaction(s), whose spectral changes are shown in Fig. 3, as confirmed by the deviation from linearity of an ED-diagram, suggesting the occurrence of photocycloaddition. ^{1}H-NMR analysis of the photoproducts showed that the intensity of the olefinic protons due to the sum of the *E*- and *Z*-isomers is reduced, suggesting the intramolecular cycloaddition of the cinnamoyl group.[15] Three signals appeared at 4.59, 6.13 and 6.28 ppm, but their assignment failed, because peaks expected to be observed at 4.27 and 4.43 ppm due to cyclobutane rings derived from cinnamoyl amides[17] were not detected because of the strong peaks at 3.8–4.4 ppm due to OCH_2 and $COOCH_2$ of **2**. In a way similar to 300 nm light irradiation, irradiation with 259 nm light resulted in a decrease of absorbance in the >250 nm region of *E*-type **2**, that was also similar to the case of dimer model (**5**) but the decreasing rate of the chromophore absorbance was larger.

Adsorption of 1 on a fused silica plate

A fused silica plate was immersed in a solution of **1** in THF for 5 min to perform surface adsorption of the macrocyclic compound. The amount of **1** adsorbed on the plate surface was estimated by the absorbance due to the cinnamamide. The occupied area was calculated to be 2.0 nm^2 molecule^{-1} on the assumption that the extinction coefficient (ε) of **2** in a THF solution is not much altered, which was based on the following experimental result made by our research group.[19] The CRA derivative bearing azobenzene units (Az-CRA), whose structure was the same as **1** with azobenzene instead of cinnamamide, was perfectly desorbed with ethanol solution containing 30 vol% ethanolamine from a silica plate that was prepared under the same conditions as in the case of **1**. The occupied area calculated with the azobenzene absorbance of the Az-CRA plate and the extinction coefficient in solution was almost same as that calculated with desorbed CRA. It resulted that the functional groups linking to CRA adsorbed on a silica plate are not orientated like a CPK model but are rather

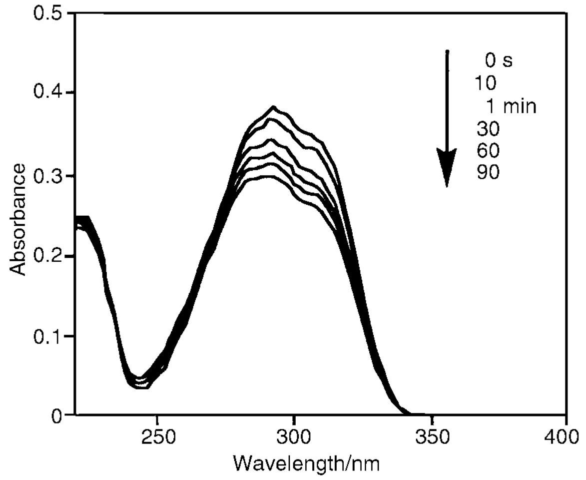


Fig. 2 UV-visible spectra of **5** as a dimer model in acetonitrile under 259 nm photoirradiation.

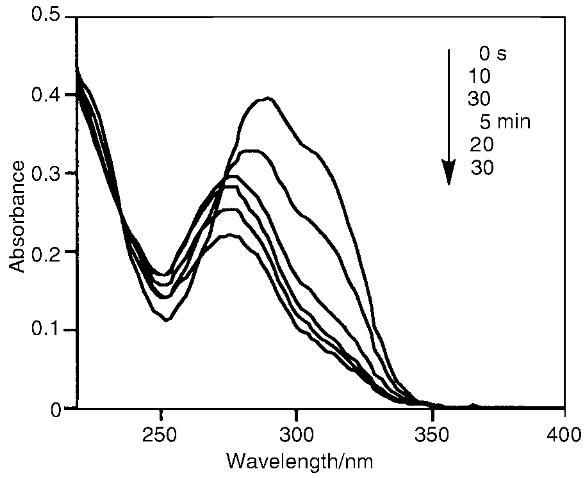


Fig. 3 UV-visible spectra of **2** in acetonitrile under 300 nm photoirradiation.

random. Note that the area is slightly larger than the base area of CRA-CM derivative (1.8 nm^2 molecule^{-1}) which is estimated by a molecular model and π–A isotherm measurements,[8] indicating that **1** forms a densely packed SAM though the molecule possesses a complicated chemical structure.

Photoreaction of 1 adsorbed on a fused silica plate

UV-visible absorption spectral changes of **1** adsorbed on the silica plate under irradiation with 300 nm light are shown in Fig. 4. The appearance of isosbestic points at the early stage within 30 s implies the predominant occurrence of *E*-to-*Z* photoisomerization. In contrast to the solution photochemistry of **2**, prolonged irradiation resulted in the gradual disappearance of the absorption band centered at about 300 nm due to the *Z*-isomer, suggesting that the chromophores suffer from photodimerization. Irradiation with 330 nm light caused also the gradual disappearance of the band, though the rate was much slower when compared with the 300 nm irradiation. This is probably because the photodimerization proceeds more efficiently upon excitation with 300 nm light. The involvement of the two photoreactions, photoisomerization and photodimerization, was confirmed by ED-diagram analysis of the spectral changes. This situation is also supported by the fact that spectral changes of the monolayer are quite similar to those of **2** in solution shown in Fig. 3. It is reasonable to assume that the photocycloaddition occurs in the SAM not only intramolecularly, but also intermolecularly on account of the dense packing of the macrocyclic compound.

Desorption of 1 from a fused silica plate

Desorption of **1** from silica plates before and after photoirradiation was followed by monitoring absorbances at $\lambda_{\max}$ of the cinnamoyl after rinsing silica plates in ethanol ultrasonically. Fig. 5 shows spectral alterations of the plates exposed to 300 nm light before and after rinsing with ethanol as a function of exposure period. The results show essentially no change in spectral shapes before and after ultrasonic treatment in ethanol, suggesting that the chemical structure is not much different between adsorbed and desorbed molecules. The desorption behavior of **1** was also examined after irradiation with light at 259 and 330 nm, respectively. Table 1 summarizes the ratio of desorbed **1** to the initially adsorbed **1** on a fused silica plate under various irradiation conditions. The fact that 33% of **1** is not desorbed even after the rinsing in ethanol arises from the multi-site adsorptivity of the CRA-CM compounds, as discussed in our previous paper.[8] No effect of photoirradiation on enhanced desorption resistance was observed by photoirradiation for 1 min within the experimental error of 8% for the desorption ratio, irrespective of excitation wavelengths. Note here that, as seen in Fig. 5, irradiation for 1 min results in marked reduction of the absorption band of the *E*-isomer owing to photoisomerization and gives rise to no significant decrease of absorbances at about 270 nm due to the *Z*-isomer.

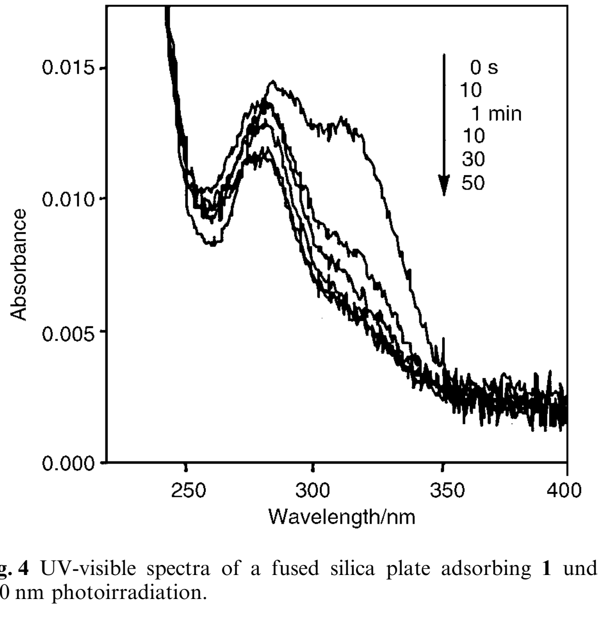


Fig. 4 UV-visible spectra of a fused silica plate adsorbing **1** under 300 nm photoirradiation.

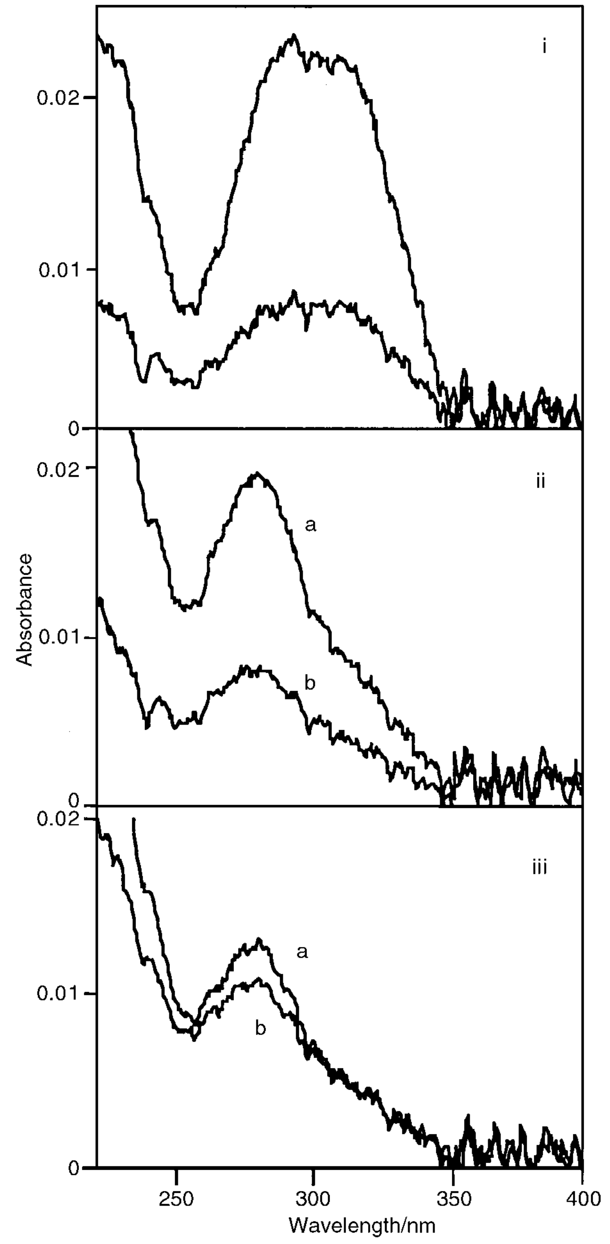


Fig. 5 UV-visible spectra of a fused silica plate adsorbing **1**, which was irradiated with 300 nm light for (i) 0 min, (ii) 1 min and (iii) 30 min (a) before and (b) after ultrasonic treatment in ethanol.

Table 1 The ratio of **1** desorbed into ethanol to **1** initially adsorbed on a silica plate[a]

	Irradiation time/min		
λ_{irr}/nm	0	1	30
259	67%	59%	17%
300		66%	19%
330		75%	55%

[a] Experimental error : ±8%.

These facts imply that the desorption is not influenced by the isomerism of the cinnamoyl group of **1** because the adsorptivity is determined specifically by the carboxy residues as polar heads. Consequently, the photoirradiation for 1 min does not display any suppressive effect on the desorption. When surface-modified plates were exposed to 259 or 300 nm light for 30 s, the desorption was sufficiently suppressed, whereas prolonged irradiation with 330 nm light exhibited scarcely any effect on the desorption resistance. As stated above, 330 nm excitation leads to photodimerization, which occurs efficiently when irradiation is made at shorter wavelengths of 259 and 300 nm, respectively. These results indicate that the desorption resistance comes from the intermolecular photodimerization of the cinnamoyl residues to enhance molecular weights of adsorbed molecules so that the number of adsorption sites increases significantly. The possibility that the enhanced desorption resistance arises from intramolecular photocycloaddition of the double bonds may not be accepted because of the following results. A dilute THF solution of **1** was exposed to 300 nm light for 30 min in advance for intramolecular photodimerization, followed by the adsorption experiments to prepare a silica plate modified with the macrocyclic compound. As shown in Fig. 6, an absorption spectrum of the plate is quite similar to that of **1**, which was irradiated in the SAM (Fig. 5iii). The immersion of the plate in ethanol resulted in the desorption of 68% of the adsorbed molecules, suggesting that the intramolecular photodimerization plays no role in the enhancement of desorption resistance.

Photocontrol of liquid crystal alignment by 1

Extensive studies have been carried out on command surfaces, which display the photocontrol of alignment of liquid crystal (LC) systems. It has already been reported that SAMs fabricated by the surface adsorption of photoreactive molecules such as azobenzenes on silica plates through hydrogen bonds are capable of controlling LC alignment by photoirradiation.[20–22] Although the SAM preparation by means of hydrogen bonding is convenient due to the simple preparative procedures, the photoreactive monolayers deposited on substrate plates through noncovalent bonds are of insufficient reliability from practical viewpoints because of partial desorption of the photoreactive molecules, which act as contaminants. Cinnamate moieties have been employed as photoreactive units for the photocontrol of LC alignment, they have been attached to polymer backbones to prepare thin polymeric films and tethered to a silica substrate surface through silylation. In this context, the macrocyclic compound **1** is of great interest, since photoirradiation plays dual roles in the LC photoalignment control due to the photoreactions and the enhanced desorption resistance of the SAMs, which are readily prepared, as shown above. This situation led us to achieve the photoalignment control of LC by photoirradiated SAM of **1**.

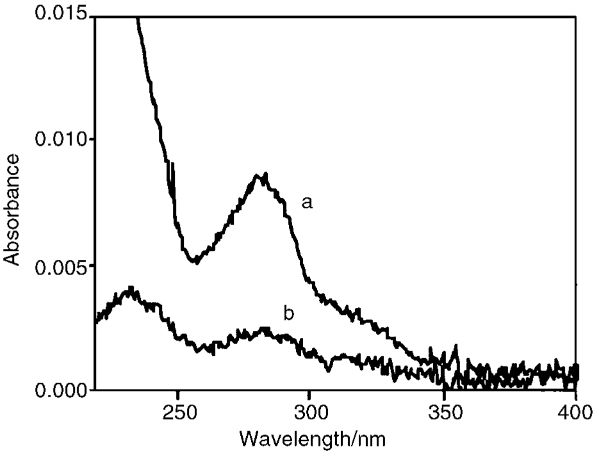


Fig. 6 UV-visible spectra of a fused silica plate adsorbing **1**, which was irradiated with 300 nm light in a dilute THF solution in advance (a) before and (b) after ultrasonic treatment in ethanol.

Cell fabrication was made by employing a silica plate adsorbing **1** and a silica plate surface-modified with lecithin for homeotropic LC alignment. Before UV irradiation, the hybrid cell exhibited random planar alignment, indicating that the SAM of **1** induces planar alignment. When the cell was exposed to 290–390 nm light from a super-high pressure mercury arc through a photomask for 20 min, LC alignment in photoirradiated areas became homeotropic. A polarized microscope demonstrated photopatterning as given in Fig. 7. The photopattern was not altered at all even after heating the cell at 60 °C above the transition temperature of the LC for 2 h. The thermostability arises not only from the photodimerization leading to the suppressive effect on orientational relaxation,[15] but also from the desorption resistance.

Conclusions

The cinnamoyl derivative (**4**) as a monomer model compound exhibits solely *E*/*Z* photoisomerization in solution in the excitation wavelength range from 259 through to 330 nm. In contrast to this, the photochemistry of a dimer model compound (**5**) and the octaester of **1** (**2**) in dilute solutions displayed marked wavelength dependence. Compound **5** undergoes not only the photoisomerization, but also intramolecular photodimerization when irradiation of its dilute solution was made at 259 nm, whereas photodimerization hardly occurred upon irradiation with light at 300 and 330 nm. The octaester of **1** (**2**) in a dilute solution suffered also from the

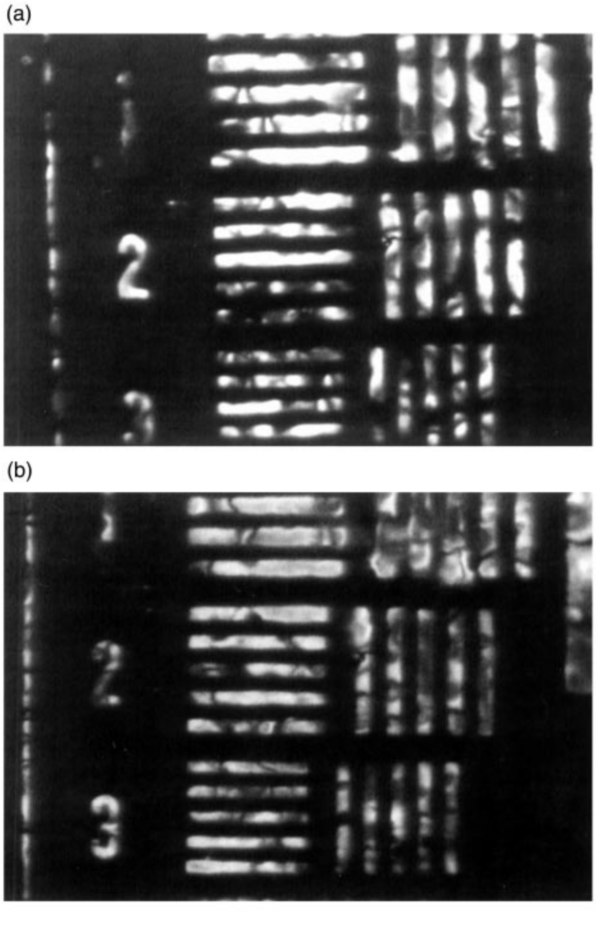


Fig. 7 Polarized micrographs of a nematic liquid crystal cell, the surface walls of which were modified with **1** after photoirradiation with 290–390 nm light through a photomask (a) before and (b) after heating at 60 °C for 2 h.

photoisomerization accompanied by a side reaction, which may be intramolecular photodimerization, when irradiation was performed with light in the wavelength region of 259–300 nm, and the excitation with 330 nm light caused essentially only the photoisomerization.

SAM of **1** with a relatively dense packing was fabricated simply by immersing a fused silica plate in a dilute solution of **1**. In contrast to the photochemistry of **2** in dilute solution, irradiation of the SAM of **1** with light not only in the range of 259–300 nm, but also at 330 nm resulted in the concurrence of a side reaction, which is likely to be intra- and intermolecular photodimerization. The desorption behavior of the SAM from the silica plate was examined before and after photoirradiation to reveal that the desorption resistance is markedly enhanced by photoirradiation because of the intermolecular photodimerization of the cinnamoyl units to increase molecular weights of the adsorbate. The effect of intermolecular photodimerization on the enhancement of desorption resistance was confirmed by the fact that no enhancement of desorption resistance was obtained when the SAM preparation was achieved after photoirradiation of a dilute solution of **1** to cause intramolecular photodimerization along with photoisomerization.

The present procedure for the preparation of SAMs having the photodimerizable units was applied to photocontrol of LC alignment. Photoirradiation resulted in transformation of LC alignment from homeotropic into planar orientation, and the LC photoalignment exhibited reasonable thermostability probably due to the photoisomerization leading to the desorption resistance.

References

1 H. Schneider, D. Guttes and U. Schneider, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 647.
2 Y. Aoyama, Y. Tanaka and S. Sugahara, *J. Am. Chem. Soc.*, 1989, **111**, 5397.
3 D. Cram, *Nature*, 1992, **356**, 29.
4 A. G. S. Hogberg, *J. Am. Chem. Soc.*, 1980, **102**, 6046.
5 L. Abis, E. Dalcanale, A. Du vosel and S. Spera, *J. Org. Chem.*, 1988, **53**, 5475.
6 M. Ueda, N. Fukushima and K. Ichimura, *J. Mater. Chem.*, 1995, **5**, 1007.
7 M. Ueda, N. Fukushima and K. Ichimura, *J. Mater. Chem.*, 1997, **7**, 641.
8 E. Kurita, N. Fukushima, M. Fujimaki, Y. Matsuzawa, K. Kudo and K. Ichimura, *J. Mater. Chem.*, 1998, **8**, 397.
9 K. Ichimura, N. Fukushima, M. Fujimaki, S. Kawahara, Y. Matsuzawa, Y. Hayashi and K. Kudo, *Langmuir*, 1997, **13**, 6780.
10 H. Schneider, D. Guttes and U. Schneider, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 647.
11 W. Li, V. Lynch, H. Thompson and M. A. Fox, *J Am. Chem. Soc.*, 1997, **119**, 7211.
12 S.-K. Oh, M. Nakagawa and K. Ichimura, *Chem. Lett.*, 1999, 349.
13 G. J. Fleer and J. Lyklema, in *Adsorption from Solution at the Solid/Liquid Interface*, ed. G. D. Parfitt and C. H. Rochester, Academic Press, New York, 1983.
14 E. Lindner and C. A. Dooley, *Proc. Int. Biodegradation Symp. 3rd*, 1976, 465.
15 S. Akabori, T. Kumagai, Y. Habana and S. Satou, *J. Chem. Soc,. Perkin Trans. 1*, 1989, 1497.
16 L. Leiserowitz and G. M. Schmidt, *J. Chem. Sci. A*, 1969, 2372.
17 F. D. Lewis, J. E. Elbert, A. L. Upthagrove and P. Hale, *J. Org. Chem.*, 1991, **56**, 553.
18 G. Gauglitz, in *Studies in Organic Chemistry 40: Photochromism, Molecules and Systems*, ed. H. Dürr and H. Bouas-Laurent, Elsevier, Amsterdam, 1990.
19 M. Fujimaki, Doctoral thesis, Tokyo Institute of Technology, 1998.
20 K. Ichimura, Y. Suzuki, T. Seki, A. Hosoki and K. Aoki, *Langmuir*, 1988, **4**, 1214.
21 Y. Kawanishi, T. Tamaki, M. Sakuragi, T. Seki and K. Ichimura, *Langmuir*, 1992, **8**, 2061.
22 K. Ichimura, Y. Akita, H. Akiyama, Y. Hayashi and K. Kudo, *Jpn. J. Appl. Phys. Part 2*, 1996, **35**, L992.