



# Convenient Preparation of Self-Assembled Monolayers Derived from Calix[4]resorcinarene Derivatives Exhibiting Resistance to Desorption

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**Abstract.** Crown conformers of *O*-carboxymethylated calix[4]resorcinarenes (CRA-CMs) bearing four perfluorooctyl- and octylazobenzene residues at the lower rim of the cyclic skeleton were synthesized to investigate the resistance to desorption of CRA-CMs forming self-assembled monolayers on aminosilylated silica substrates and the surface energy photocontrol based on *E-to-Z* photoisomerization of the azobenzene moiety. In comparison with CRA-CM monolayers on silica substrates, the desorption of CRA-CMs on the aminated substrate was remarkably suppressed even when CRA-CM monolayers were sonicated in polar solvents and even in water. The high desorption-resistance was attributable to multi-point adsorption of CRA-CMs through COOH/NH<sub>2</sub> interactions. UV-Vis spectral studies revealed that CRA-CM substituted with *p*-octylazobenzene exhibited high *E-to-Z* photoisomerizability up to 92% in self-assembled monolayers, while less photoisomerizability was observed for CRA-CM bearing *p*-perfluorooctylazobenzenes due to the steric hindrance of the larger perfluoroalkyl chains. Photoinduced changes of contact angles for water up to 8.3° were observed for a CRA-CM monolayer.

**Key words:** calix[4]resorcinarene, self-assembled monolayer, photoisomerization, aminosilanization, chemisorption

## 1. Introduction

The photo-switchable properties of photochromic molecules including molecular shapes, electronic spectra, dipole moments etc., have attracted extensive interest because of their versatile applicability to manipulate molecular systems incorporating photochromic molecules as phototriggers [1]. We have focused our attention so far on self-assembled monolayers (SAMs) bearing photochromic molecules as working surfaces (command surfaces) leading to marked molecular amplification, such as surface-assisted photocontrol of liquid crystal alignment and of dispersibility of colloidal silica [2–3]. In the command surfaces, photoinduced structural as well as orientational transformation of the outermost molecular layers determines

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critically the extent and efficiency of these kinds of surface-assisted phenomena. In this context, a sufficient free volume in SAMs is required to display high photoisomerizability of photochromic molecular triggers. Usually, self-assembled monolayers are formed as a result of effective *van der Waals* interactions among long-chain alkyl residues so that molecular building blocks are densely packed to reduce the two-dimensional free volume considerably. In order to optimize the surface-assisted photocontrol of the molecular systems, photo-reactive SAMs possess the following contradictory conditions. SAMs should be densely packed as much as possible to cover a bare surface of substrate, whereas a free volume required for photoisomerization should be ensured sufficiently. Taking notice of these requirements, we employed a crown isomer of a calix[4]resorcinarene (CRA) as a building block for the fabrication of a photo-reactive SAM. CRA possesses eight hydrophilic residues at the upper rim of the cyclic skeleton [4], while hydrophobic residues are tethered to the lower rim. In this respect, CRAs are referred to as macrocyclic amphiphiles. It is worthy to mention that the cross-sectional area of the base of CRA ( $\approx 1.3 \text{ nm}^2$ ) is larger than the sum of that of four alkyl residues and that the base area can be enlarged by the modification of the phenolic OH groups by *O*-carboxymethylation or *O*-hydroxyethylation, as discussed in our previous paper [3]. It was revealed that CRA and its *O*-carboxymethylated (CRA-CMs) and *O*-hydroxyethylated derivatives adsorb on polar surfaces such as silica surfaces from their dilute solutions to form densely packed monolayers due to the formation of multi-point adsorption through hydrogen bondings between the macrocyclic amphiphiles and the polar surfaces [3, 5, 6]. It should be stressed that the molecular packing in this kind of SAMs is determined specifically by the base area of the macrocyclic amphiphiles so that a free volume exists more or less in molecular layers consisting of hydrophobic residues attached to the lower rim of the cyclic skeletons. This situation was confirmed by the evaluation of the *E-to-Z* photoisomerizability of azobenzene moieties which are introduced to the lower rim [5, 6].

The procedure to prepare SAMs using CRA derivatives is very simple and convenient, but has a drawback for some purposes. Since the resulting SAMs are formed through hydrogen bonding between the polar heads and a silica surface, the exposure to polar solvents including water resulted in partial desorption of the macrocyclic amphiphiles to deteriorate the SAMs [3]. In order to extend the applicability of the SAM preparation using CRA derivatives, it is essential to overcome such a problem. To improve the resistance toward desorption induced by polar solvents, we chose COOH/NH<sub>2</sub> interactions which are stronger than COOH/silanol interactions to fabricate SAMs derived from CRA-CM. We report here that the desorption of CRA-CMs forming densely packed monolayers is remarkably suppressed by COOH/NH<sub>2</sub> interactions in addition to multi-point adsorption when a silica substrate is modified with an aminosilylating agent.

## 2. Experimental

### 2.1. MATERIALS

4-(4-Perfluorooctylphenylazo)phenol and 4-(4-octylphenylazo)phenol were prepared through azo-coupling reactions from 4-perfluorooctylaniline [7] and 4-octylaniline, respectively. 2,8,14,20-Tetrakis(3-iodopropyl)-4,6,10,12,16,18,22,24-octakis(ethoxycarbonylmethoxy)calix[4]arene (I-CRA-EtCM) was prepared according to our previous paper [6]. All other chemicals were purchased from Aldrich and used without further purification.

#### 2.1.1. 2,8,14,20-Tetrakis[3-[4-(4-perfluorooctylphenylazo)phenoxy]propyl]-4,6,10,12,16,18,22,24-octakis(carboxymethoxy)calix[4]arene (F-CRA-CM)

To a solution of I-CRA-EtCM (0.65 g, 0.35 mmol) in anhydrous DMF (30 mL) were added 4-(4-perfluorooctylphenylazo)phenol (0.95 g, 1.54 mmol) and dried  $K_2CO_3$  (0.21 g, 1.54 mmol). The reaction mixture was stirred at room temperature for 16 h under a nitrogen atmosphere. After ethyl acetate (150 mL) was added, the organic layer was washed with water, dried over anhydrous magnesium sulfate and subjected to column chromatography [ $SiO_2$ : ethyl acetate/hexane (1 : 1)]. The ester of F-CRA-CM of mp 153 °C as an orange powder was obtained in a 86.5% yield (1.15 g) after recrystallization from 2-propanol [Anal. Calcd. for  $C_{152}H_{124}N_8O_{28}F_{68}$ : C, 48.01; H, 3.29; N, 2.95. Found: C, 48.03; H, 3.31; N, 2.95.  $^1H$  NMR ( $CDCl_3$ , 200 MHz)  $\delta$ : 1.29 (24H, t,  $J = 7.0$  Hz), 1.82–2.03 (8H, m), 2.04–2.28 (8H, m), 3.96–4.11 (8H, m), 4.22 (16H, q,  $J = 7.0$ ), 4.32 (16H, s), 4.77 (4H, t,  $J = 6.7$ ), 6.27 (4H, s), 6.79 (4H, s), 6.87 (8H, d,  $J = 9.0$ ), 7.61 (8H, d,  $J = 8.6$ ), 7.77 (8H, d,  $J = 9.0$ ), 7.84 (8H, d,  $J = 8.6$ )]. To a solution of the esterified F-CRA-CM (0.30 g, 0.08 mmol) in THF (20 mL) was added an aqueous solution (12 mL) of KOH (0.24 g, 4.28 mmol). After stirring at room temperature for 1 h, the reaction mixture was acidified up to pH = 3 with dilute hydrochloric acid. An organic layer was extracted with a mixture of diethyl ether (18 mL) and THF (10 mL) and washed with water. The solution was concentrated and dried in vacuo at 50 °C to afford 0.27 g (95.7%) of F-CRA-CM as an orange powder (mp > 300 °C). Anal. Calcd. for  $C_{136}H_{92}N_8O_{28}F_{68}$ : C, 45.65; H, 2.59; N, 3.13. Found: C, 45.54; H, 2.80; N, 3.06.  $^1H$  NMR ( $THF-d_8$ , 200 MHz)  $\delta$ : 1.82–2.07 (8H, m), 2.08–2.28 (8H, m), 4.14 (8H, t,  $J = 5.3$  Hz), 4.21–4.47 (16H, m), 4.85 (4H, t,  $J = 6.6$ ), 6.45 (4H, s), 6.83 (4H, s), 6.98 (8H, d,  $J = 9.0$ ), 7.71 (8H, d,  $J = 8.4$ ), 7.81 (8H, d,  $J = 9.0$ ), 7.93 (8H, d,  $J = 8.4$ ).  $^{19}F$  NMR ( $THF-d_8$ , 188 MHz)  $\delta$ : -76.8, -105.9, -117.3, -121.9. FT-IR (KBr,  $cm^{-1}$ ): 1736 (C=O).

#### 2.1.2. 2,3,14,20-Tetrakis[3-[4-(4-octylphenylazo)phenoxy]propyl]-4,6,10,12,16,18,22,24-octakis(carboxymethoxy)calix[4]arene (H-CRA-CM)

H-CRA-CM with four octylazobenzene units was prepared similarly to F-CRA-CM from I-CRA-EtCM and 4-(4-octylphenylazo)phenol: orange powders (96.2%

yield), mp > 300 °C. Anal. Calcd. for  $C_{136}H_{160}N_8O_{28} \cdot 3H_2O$ : C, 67.81; H, 6.95; N, 4.65. Found: C, 67.56, H, 6.82; N, 4.41.  $^1H$  NMR (DMSO- $d_6$ , 200 MHz)  $\delta$ : 0.83 (12H, t,  $J = 6.8$  Hz), 1.03–1.40 (40H, m), 1.42–1.66 (8H, m), 1.67–1.90 (8H, m), 1.92–2.20 (8H, m), 2.55 (8H, t,  $J = 7.2$ ), 3.88–4.13 (8H, m), 4.19–4.58 (16H, m), 4.64–4.80 (4H, m), 6.48 (4H, s), 6.82 (4H, s), 6.91 (8H, d,  $J = 9.0$ ), 7.17 (8H, d,  $J = 8.4$ ), 7.60 (8H,  $J = 8.4$ ), 7.67 (8H, d,  $J = 9.0$ ), FT-IR (KBr,  $cm^{-1}$ ): 1736 (C=O).

## 2.2. FABRICATION OF CHEMISORBED CRA-CM MONOLAYERS

Fused silica substrates were ultrasonically cleaned in a piranha solution for 1 h (**WARNING:** Piranha solution should be handled with caution; it detonates unexpectedly.) [8]. The substrates were washed with deionized water, thoroughly rinsed with acetone and dried under vacuum prior to use. Cleaned silica substrates ( $SiO_2$ ) were immersed in a solution of freshly distilled 3-aminopropyltriethoxymethylsilane (0.25 g) in anhydrous toluene (25 g) at 25 °C for 30 min. The substrate were washed with dry toluene, baked in an oven at 120 °C for 30 min, sonicated in toluene and methanol for 2 min and dried under vacuum to obtain aminated substrates. The aminated substrates ( $NH_2/SiO_2$ ) were immersed in a THF solution of  $1 \times 10^{-4}$  mol  $dm^{-3}$  CRA-CM at 40 °C for 30 min. SAMs (CRA-CM/ $NH_2/SiO_2$ ) were obtained after rinsing with THF and drying at 80 °C for 30 min. CRA-CM monolayers on silica substrates (CRA-CM/ $SiO_2$ ) were prepared after a similar work-up.

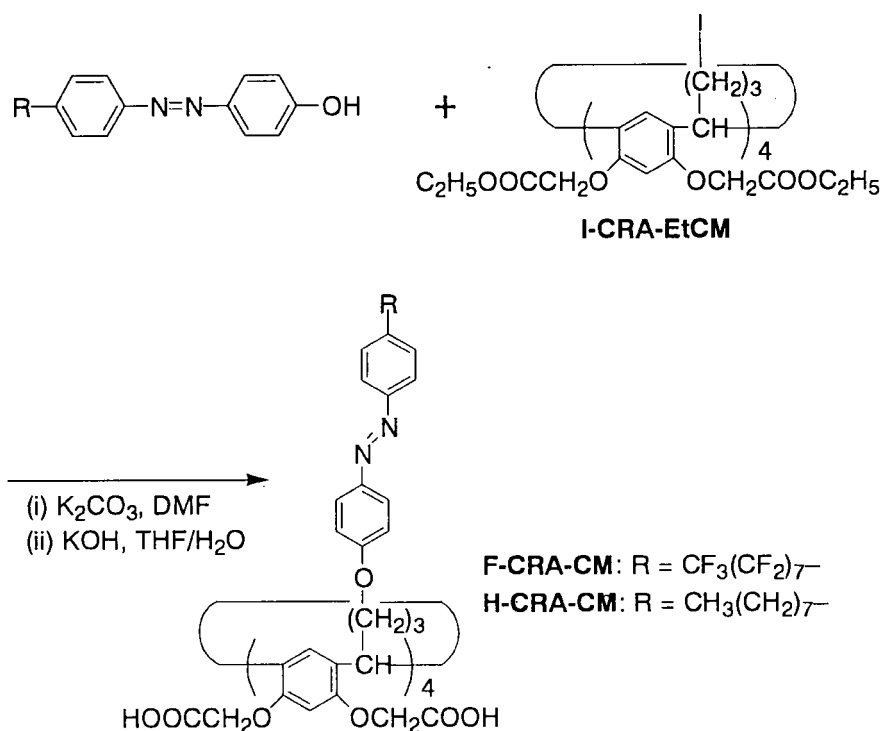
## 2.3. PHYSICAL MEASUREMENTS

UV-Vis absorption spectra for chemisorbed monolayers were recorded on a JASCO MAC-1 weak absorption spectrophotometer. Contact angles for water or hexadecane drops were measured on a contact angle meter (CA-X, Kyowa Interface Science Co., Ltd.). Irradiation of CRA-CM chemisorbed monolayers was performed using UV light (365 nm) and blue light (436 nm) separated from a Hg-Xe lamp.

# 3. Results and Discussion

## 3.1. SYNTHESIS AND FABRICATION OF CHEMISORBED MONOLAYERS

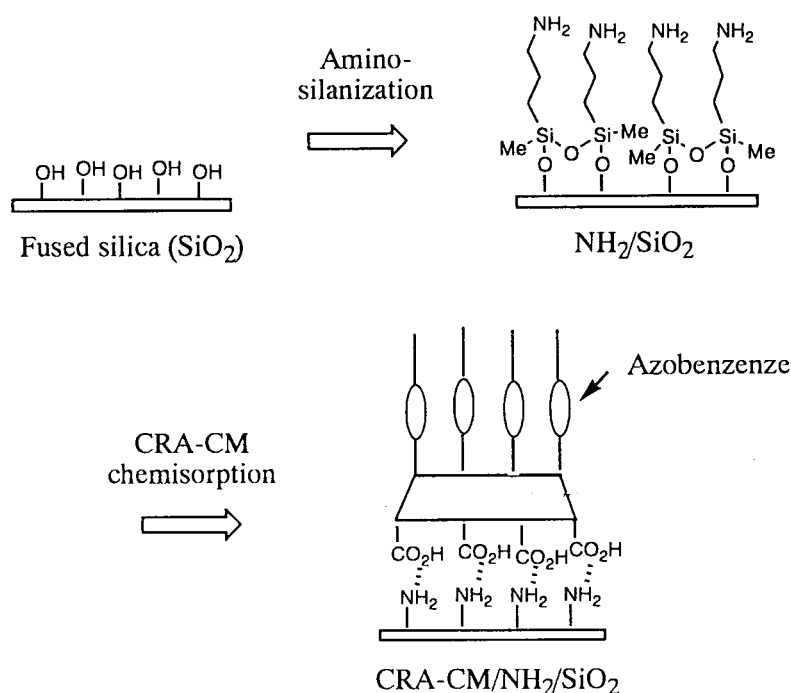
*O*-Carboxymethylated calix[4]resorcinarene derivatives (CRA-CMs) with azobenzene residues were used in this study because the azobenzene moieties are convenient to monitor adsorption and desorption behavior of CRA-CMs spectroscopically. Perfluorooctyl and octyl substituents were employed to operate reversible changes of hydrophilicity and lipophilicity caused by photoisomerization of the azobenzene core upon UV light irradiation. As stated in our previous paper [6], the crown isomer of *O*-carboxymethoxylated calix[4]resorcinarene (I-CRA-EtCM) with iodopropyl substituents is a convenient compound to synthesize a series of



Scheme 1. Preparation of calix[4]resorcinarene derivatives (F-CRA-CM and H-CRA-CM).

calix[4]resorcinarene derivatives with various functional groups. The azobenzene-modified calix[4]resorcinarenes of H-CRA-CM and F-CRA-CM having octyl and perfluorooctyl groups, respectively, were prepared through a Williamson reaction of I-CRA-EtCM, followed by alkaline hydrolysis, as shown in Scheme 1.  $^1\text{H}$  NMR data of the final products indicated that the conformation of CRA-CMs is not altered throughout the synthetic pathways and maintains a cone conformation in which eight carboxyl acid groups and azobenzene groups are tethered to their upper and lower rims, respectively. Compared with the unsubstituted azobenzene-modified CRA-CM prepared previously in our laboratory [3, 5], the introduction of perfluoroalkyl units to azobenzene moieties enhanced solubility in common organic solvents including THF, acetone and DMSO.

The fabrication of chemisorbed monolayers of CRA-CMs was carried out by immersing cleaned silica substrates in a THF solution of  $1 \times 10^{-4} \text{ mol dm}^{-3}$  CRA-CM. The occupied molecular areas of CRA-CMs in their chemisorbed monolayers were estimated to be  $14.7 \text{ nm}^2 \text{ molecule}^{-1}$  for F-CRA-CM and  $2.9 \text{ nm}^2 \text{ molecule}^{-1}$  for H-CRA-CM using UV-Vis spectroscopy under the assumption that absorption coefficients in solution are not altered in SAMs [6]. Compared with our previous study on molecular areas of the calix[4]resorcinarene skeleton ( $2.0 \text{ nm}^2 \text{ molecule}^{-1}$ ) [5, 6], these occupied areas are relatively larger. This is because of



Scheme 2. Schematic representation of CRA-CM monolayers on an aminated silica substrate.

the difficulty of self-assembly caused by their improved solubility since the adsorption of the macrocyclic amphiphiles is a reversible process.

Consequently, we employed COOH/NH<sub>2</sub> interactions for the surface adsorption, in order to fabricate densely packed SAMs of CRA-CMs on silica surfaces and to improve the resistance to desorption in polar solvents. Aminosilylated silica plates were obtained by treating fused silica substrates with a toluene solution of 3-aminopropyldiethoxymethylsilane in a conventional way [9]. The aminosilylated plates were subsequently immersed in dilute solutions of the CRA-CMs to afford densely packed chemisorbed monolayers (CRA-CM/NH<sub>2</sub>/SiO<sub>2</sub>) (Scheme 2). The occupied areas were 2.2 and 2.3 nm<sup>2</sup> molecule<sup>-1</sup> for F-CRA-CM and H-CRA-CM, respectively. These values are not far from the base area of CRA-CM (1.7 nm<sup>2</sup>) even though the molecules possess four bulky and complicated substituents.

### 3.2. RESISTANCE TO DESORPTION

Figure 1 shows the desorption behavior of CRA-CMs adsorbed on a virgin silica plate and an aminated silica plate after sonication of the plates in water at 25 °C. For CRA-CM/SiO<sub>2</sub>, absorbances of the azobenzene decreased considerably after the sonication. On the other hand, no desorption was observed for CRA-CM/NH<sub>2</sub>/SiO<sub>2</sub> even after sonication in water for 1 h. Table I summarizes the desorption-resistance

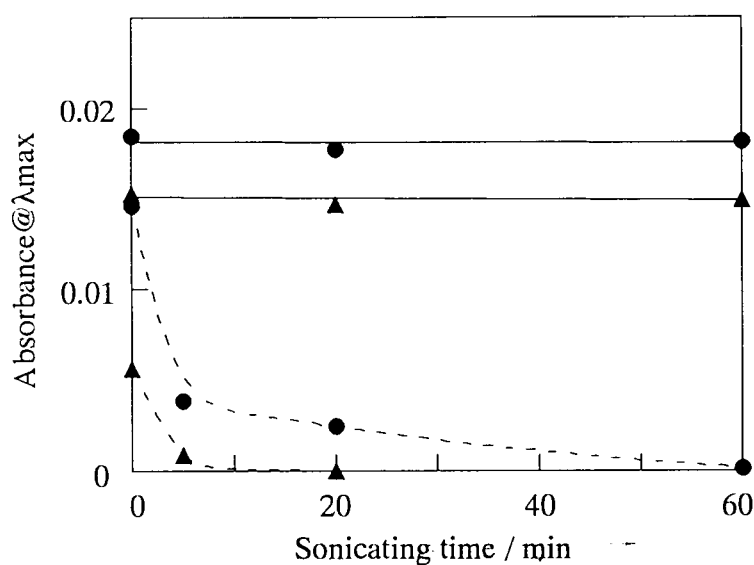


Figure 1. Absorbance changes of CRA-CM monolayers as a function of sonication time in water (25 °C): F-CRA-CM (triangle) and H-CRA-CM (circle) on silica (dashed line) and aminated silica substrate (solid line).

Table I. Desorption-resistance of CRA-CMs forming monolayers in organic solvents

Solvent	Resistance to desorption (%) <sup>a</sup>			
	Silica substrate		Aminate substrate	
	F-CRA-CM	H-CRA-CM	F-CRA-CM	H-CRA-CM
Ethanol	30	10	100	100
THF	60	0	100	95
Hexane	100	100	100	100
10 wt% ethanolamine in ethanol <sup>b</sup>	n.d.	n.d.	10	10

<sup>a</sup> The percentages indicate the remaining amounts of CRA-CM estimated from absorbance at  $\lambda_{\max}$  after sonication for 20 min.

<sup>b</sup> Sonication duration is 10 min.

in polar organic solvents such as ethanol and THF. CRA-CMs on silica substrates were readily detached not only in water, but also in polar organic solvents, whereas essentially no desorption took place for CRA-CMs adsorbed on an aminated silica substrate after sonication for 20 min. No desorption occurs in nonpolar hexane for CRA-CMs adsorbed on both silica and aminated silica substrates. Detachment of CRA-CM is induced efficiently by treatment a basic ethanol solution containing ethanolamine.

The extraordinary acidity of carboxy groups [10] and the basicity of amino groups [11] in self-assembled monolayers were reported. The direct observa-

tion of  $\text{—NH}_3^+\text{—OOC—}$  ion pairs was achieved using FTIR spectroscopy by Liu et al., using a Langmuir–Blodgett composite monolayer comprising amphiphilic azobenzene-modified alkylcarboxylic acid and aminoethanethiol on gold substrates [12]. These results imply that the amino groups on an outermost surface of  $\text{NH}_2/\text{SiO}_2$  and the carboxy groups at the upper rim of CRA-CMs hold together by ion pairing in addition to *van der Waals* interactions and hydrogen bonds. This explanation is supported by the fact that most of the CRA-CM was washed off after treatment with the ethanolamine solution. Another important factor to result in the strong adsorption of CRA-CM on animated substrates may involve the capability of multi-point adsorption due to the eight carboxy groups. In order to confirm the cooperativity of the multi-point adsorption of CRA-CMs, the adsorption and desorption behavior of 10-[4-(4-hexylphenylazo)phenoxy]decanoic acid as a model compound was investigated using the aminated substrate ( $\text{NH}_2/\text{SiO}_2$ ). The adsorption amounts of the model compound were much smaller than those of CRA-CMs even when the adsorption was carried out from nonpolar hexane and toluene. Furthermore, the desorption behavior of the adsorbates toward water was observed. These experimental results support the suggestion that the strong adsorption and the resistance toward desorption result from the multi-point adsorptivity of the macrocycles through  $\text{COOH}/\text{NH}_2$  interactions in CRA-CM/ $\text{NH}_2/\text{SiO}_2$  monolayers.

### 3.3. *E/Z* PHOTOISOMERIZATION IN MONOLAYERS

Figure 2 shows UV-Vis spectral changes of F-CRA-CM and H-CRA-CM in THF solutions and in the monolayers on  $\text{NH}_2/\text{SiO}_2$  substrates upon irradiation of 365 nm light. Azobenzene moieties in an H-CRA-CM monolayer exhibit high *E-to-Z* photoisomerizability up to 92%, which was almost consistent with that of 99% in a THF solution. The high photoisomerizability was similar to that of our previous observation for CRA-CM bearing unsubstituted azobenzene residues and 4-cyclohexylazobenzene residues [5], indicating that a sufficient free volume in the SAM is ensured for *E-to-Z* photoisomerization of the azobenzenes in SAMs in spite of their densely packed structuring. A striking result worth describing was observed for F-CRA-CM/ $\text{NH}_2/\text{SiO}_2$  monolayers. The level of *E-to-Z* conversion of the perfluorooctylazobenzene moieties was ca. 65% upon 365 nm irradiation. It is very likely that the reduction of the photoisomerizability of F-CRA-CM in a monolayer stems from a larger cross-section area of perfluorocarbon units (ca.  $0.29 \text{ nm}^2$  [13]) than that of hydrocarbon units (ca.  $0.20 \text{ nm}^2$  [14]) leading to the enhancement of intermolecular and/or intramolecular steric hindrance.

### 3.4. PHOTOCONTROL OF SURFACE ENERGY

The preparation of SAMs of CRA-CMs on aminated silica substrates exhibiting high desorption-resistance toward polar solvents enabled us to carry out reliable measurements of contact angles for water before and after photoirradiation. Table II



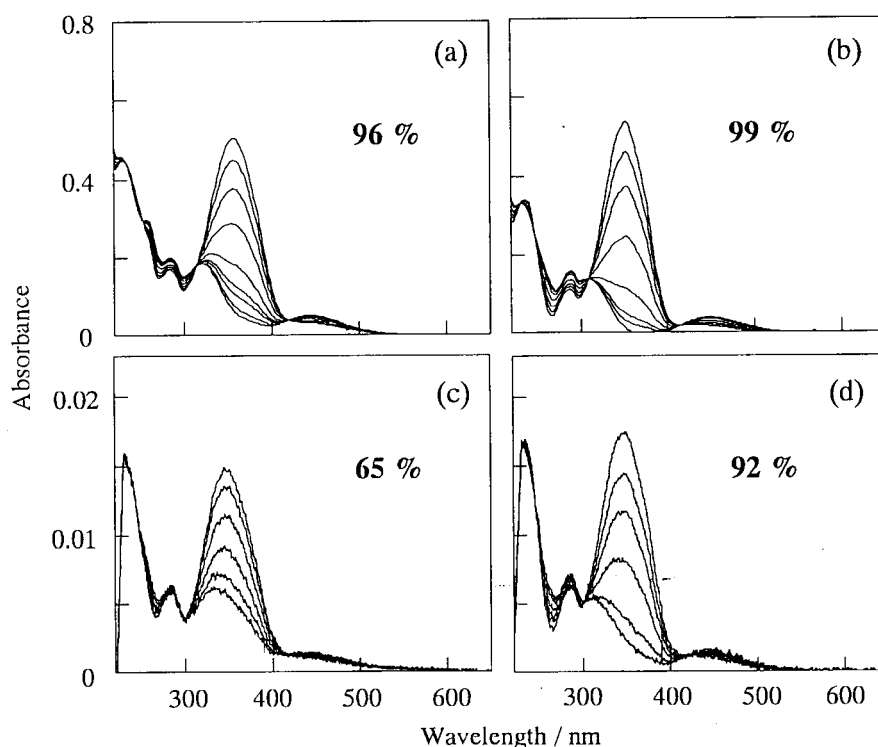


Figure 2. UV-Vis spectral changes of (a) F-CRA-CM in THF, (b) H-CRA-CM in THF, (c) F-CRA-CM/NH<sub>2</sub>/SiO<sub>2</sub> and (d) H-CRA-CM/NH<sub>2</sub>/SiO<sub>2</sub> on irradiation with 365 nm light: Inset percentages indicate the conversion percentages to Z-isomer at photostationary state.

lists contact angles of water and hexadecane for the CRA-CM/NH<sub>2</sub>/SiO<sub>2</sub> monolayers before and after irradiation of 365 nm light. Before UV irradiation, contact angles for water and hexadecane on a SAM of H-CRA-CM (CRA-CM/NH<sub>2</sub>/SiO<sub>2</sub>) were  $91.7 \pm 1^\circ$  and  $4.8 \pm 1^\circ$ , respectively. It was reported that contact angles for water and hexadecane on densely packed long-alkyl chains are  $111\text{--}115^\circ$  and  $45\text{--}46^\circ$  [15]. Consequently, the reduced contact angles on CRA-CM/NH<sub>2</sub>/SiO<sub>2</sub> reflect that the packing of octyl chains attached to the azobenzene of H-CRA-CM is disordered due to the larger cross-sectional area of the CRA-CM units which determine the packing density, being in line with the high level of *E-to-Z* photoisomerization. The larger contact angles of  $104.3 \pm 1^\circ$  and  $57.9 \pm 1^\circ$  for water and hexadecane, respectively, on a SAM of F-CRA-CM, compared with those of that of H-CRA-CM, indicate that perfluorooctyl residues are exposed to a water phase at the outermost surface of the CRA-CM/NH<sub>2</sub>/SiO<sub>2</sub>.

A relatively large decrease in a contact angle for water was observed on a SAM of H-CRA-CM after *E-to-Z* photoisomerization. The difference of contact angle before and after UV-irradiation was  $8.3^\circ$ . This value is larger than that (ca.  $6^\circ$ ) for a monolayer prepared by the silylation of a silica surface with a silylating

Table II. Contact angles of water and hexadecane for CRA-CM/NH<sub>2</sub>/SiO<sub>2</sub> before and after irradiation with 365 nm light

CRA-CM	Contact angle (degree)			$\Delta\theta$
	Liquid	<i>E</i> -form	<i>Z</i> -form	
F-CRA-CM	Water	104.3 ± 1	103.8 ± 1	0.5
	Hexadecane	57.9 ± 1	55.4 ± 1	2.5
H-CRA-CM	Water	91.7 ± 1	83.4 ± 1	8.3
	Hexadecane	4.8 ± 1	0	4.8

reagent incorporating a *p*-hexylazobenene unit, as reported previously [16]. It is very likely that this situation may arise both from the efficient photoisomerizability of H-CRA-CM in a monolayer and from the preference of perpendicular orientation of the azobenzene units owing to the characteristic molecular structure of CRA-CM, in which the azobenzene chromophores stretched out in the same direction. A considerable increment of lipophilicity of the SAM of H-CRA-CM by UV-irradiation is again caused by the enhanced disordering of the octyl chains of *Z*-isomer. On the other hand, a photo-induced change in the contact angle for water on a SAM of F-CRA-CM was negligibly small. Although the level of *E-to-Z* photoisomerization of F-CRA-CM in SAM is lower than that of H-CRA-CM as stated above, the insensibility to the photoirradiation stems rather from the situation that perfluorooctyl substituents remain exposed to a surface of SAM even after the photoisomerization because of the peculiarity of perfluoroalkyls giving a lower surface energy.

In summary, we developed a novel and simple way to prepare photo-reactive SAMs with high resistance to desorption in polar solvents by using COOH/NH<sub>2</sub> interactions. This technique provides a procedure to fabricate tailor-made monolayers ensuring a free volume required for photoisomerization. A high level of *E-to-Z* photoisomerizability of azobenzenes was attained in densely packed monolayers even though the azobenzene chromophore is substituted with the bulky octyl group and gave rise to the efficient photocontrollability of surface energy. The present procedure for SAM preparation will play a significant role in the photocontrol of versatile interfacial phenomena.

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