Self-Assembled Monolayers Derived from Calix[4]resorcinarenes Exhibiting Excellent Desorption-Resistance and Their Applicability to Surface Energy Photocontrol

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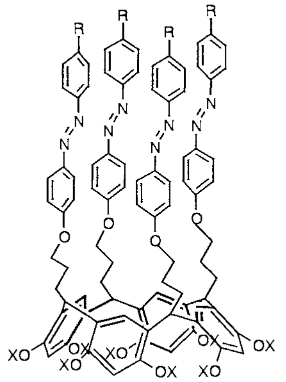
Self-assembled monolayers exhibiting excellent desorption-resistance was readily available by the adsorption of crown conformers of *O*-carboxymethylated calix[4]resorcinarenes on aminated silica substrates through multi-point adsorption.

Self-assembled monolayers (SAMs) are prepared by surface adsorption to offer fundamental understanding of interfacial phenomena and to provide unlimited possibilities for applications in various fields.[1] From both of fundamental and practical viewpoints, their enhanced stability toward desorption is highly required. Recently we have described the adsorption of crown conformers of calix[4]resorcinarenes (CRAs) and their *O*-octacarboxymethylated derivatives (CRA-CMs) on a silica surface through hydrogen bonding to give rise to densely packed SAMs[2] and the application to prepare photofunctional monolayers incorporating azobenzene residues.[3] The procedure to give this type of SAMs is very simple and convenient, but there have been a drawback for some purposes. Since the resulting SAMs are formed through hydrogen bonds 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 structure of SAMs.[2] An exceptional example is a CRA substituted with sugar residues at eight phenolic OH groups, which adsorbs on a silica plate even in an aqueous solution.[4] In order to extend the applicability of the SAM architecture using CRA families, it is essential to overcome the desorption problem. We report here that the desorption of CRA-CMs forming densely packed monolayers is remarkably suppressed by $COOH/NH_2$ interactions in addition to the multi-point adsorption when a silica substrate is modified with an aminosilylating agent.



X = CH_2COOH

1 : R = $(CF_2)_7CF_3$

2 : R = $(CH_2)_7CH_3$

Aminosilylated silica plates were obtained by treating fused silica plates with a toluene solution of (3-aminopropyl)diethoxymethylsilane in a conventional way.[5,6] The CRA-CMs **1** and **2**[7] were readily adsorbed on the aminosilylated silica by immersing them in dilute solutions of the CRA-CMs.[8]

Occupied molecular areas of CRA-CMs in the chemisorbed monolayers were estimated to be 2.2 nm^2 molecule^{-1} for **1** and 2.3 nm^2 molecule^{-1} for **2**, respectively, by using UV-visible spectroscopy under assumption that their absorption coefficients in solution are not altered in SAMs.[3b] These values are not far from the base area of CRA-CM (1.7 nm^2)[9] even though the molecules possess four bulky substituents, indicating that CRA-CMs form reasonably densely packed monolayers on the aminated plates.

Table 1. Desorption-resistance of CRA-CMs forming monolayers

Solvent	Resistance to desorption of **1** (**2**) (%)[a] silica substrate	 aminated substrate
Water[b]	0 (0)	100 (100)
Ethanol	30 (10)	100 (100)
THF	60 (0)	100 (95)
Hexane	100 (100)	100 (100)
2-Aminoethanol sol.[c]	n. d.	10 (10)
TsOH sol.[d]	n. d.	0 (0)

[a] The percentages indicate the remaining amounts of CRA-CMs estimated from UV-visible absorbance changes at λ_{max} after sonication for 20 min. The values in parenthesis present the desorption-resistance of **2**. [b] Sonication was carried out for 1 h. [c] Sonication was carried out for 10 min in a 10 wt% ethanol solution of 2-aminoethanol. [d] Sonication was carried out for 10 min in an 1 wt% ethanol solution of *p*-toluenesulfonic acid.

Table 1 summarizes the desorption-resistance of CRA-CMs adsorbed on a virgin silica plate and an aminated silica plate after sonication of the plates at 25 °C in various solvents including organic acid and base solutions. CRA-CMs on silica plates were detached readily not only in water, but also in polar organic solvents, whereas essentially no desorption took place for CRA-CMs adsorbed on aminated silica substrates even after sonication. No desorption was detected in hexane for CRA-CMs adsorbed on both of silica and aminated silica substrates. However, the detachment of CRA-CM was induced outstandingly by treatment with an acidic and a basic ethanol solutions containing *p*-toluenesulfonic acid and ethanolamine, respectively. These results imply that the amino groups on an outmost surface of the aminated substrates 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. It is worthy to mention that one of the important factors to result in the strong adsorption of CRA-CMs on aminated plates may involve the capability of multi-point adsorption of their plural carboxy groups. The effect of the multi-point adsorption of CRA-CMs was confirmed by examining the desorption behavior of 10-[4-(hexylphenylazo)phenoxy]decanoic acid as a control from the aminated surface. The adsorbed monocarboxylic acid was readily washed off in polar solvents.

Grazing angle reflection-absorption infrared spectroscopy (FTIR-RAS) study was carried out on a CRA-CM monolayer adsorbed on an aminated Au substrate[10] in place of those on aminated silica plates, since the latter gave no reliable spectroscopic information. It was found that the intensity of $\nu_{C=O}$ at 1740 cm^{-1} relative to that of an internal standard band, $\nu_{as, ring\text{-}O\text{-}C}$, at 1248 cm^{-1} is significantly decreased when compared with that in a KBr pellet. This situation stems from the preferential conformation of the C=O group in parallel with the surface and/or from the ionic bonding[11] to form carboxylates due to the surface adsorption, being consistent with the enhanced desorption-resistance of the SAMs.

The azobenzene moieties in SAM of **2** on the aminated silica plate exhibited high *E-to-Z* photoisomerizability up to 92% on irradiation with 365 nm light, while a 99% conversion was attained in THF. A striking result worthy to describe was observed for a monolayer of **1**. The level of *E-to-Z* conversion of the perfluorooctylazobenzene was only *ca.* 65% upon 365 nm irradiation. It is very likely that the decrease of the photoisomerizability of **1** in a monolayer arises from the enhancement of steric hindrance of the outmost substituents because of a larger cross-sectional area of perfluoroalkyl units (*ca.* 0.29 nm^2)[12] than that of hydrocarbon units (*ca.* 0.20 nm^2).[13]

Table 2. Contact angle changes for CRA-CMs on aminated substrates before and after irradiation with 365 nm light

		Contact angle (deg)		
CRA-CM	Probe liquid	*E*-form	*Z*-form	$\Delta\theta$
1	Water	104.3	103.8	0.5
	Hexadecane	57.9	55.4	2.5
2	Water	91.7	83.4	8.3
	Hexadecane	4.8	0	4.8

SAMs of CRA-CMs on aminated silica plates were sufficiently robust toward polar solvents to carry out reproducible observation of wettability for water before and after photoirradiation. Table 2 lists contact angles for water and hexadecane on the CRA-CM monolayers on aminated substrates before and after irradiation with 365 nm light. A relatively large decrease in a contact angle for water was observed on a SAM of **2** when compared with that of **1** after *E-to-Z* photoisomerization. Though the level of *E-to-Z* photoisomerization of **1** in SAM is lower than that of **2** as stated above, the insensibility to the surface energy changes of **2** stems rather from the situation that perfluorooctyl substituents remain to be exposed to a topmost surface of SAM even after the photoisomerization. This is because of the peculiarity of perfluoroalkyls giving a lower surface energy. In the case of SAM of **1**, a larger contact angle change was observed for hexadecane than for water, in a contrast to the case of **2**. These results imply that contact angle changes triggered by the SAM of **1** reflects the enhanced disordering of the monolayer through *E-to-Z* photoisomerization, leading to the modification of dispersion interactions, whereas the increased polarity effect is also involved in the SAM of **2**.

In conclusion, a novel and simple way to prepare SAMs of CRA-CM exhibiting excellent resistance to desorption in polar solvents was explored by using COOH/NH_2 interactions. The monolayers display a high level of *E-to-Z* photoisomerizability of azobenzenes incorporated and the ability to control surface free energies by light.

References and Notes

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6 Park *et al.* indicate that the surface density of amino groups on the aminosilylated silica plates is 3.7 - 4.2 per nm^2. For a detail; see Ref. 5b.

7 4-(4-Perfluorooctylphenylazo)phenol or 4-(4-octylphenylazo)phenol was coupled with 2,8,14,20-tetrakis(3-iodopropyl)-4,6,10,12,16,18,22,24-octakis(ethoxycarbonylmethoxy)calix[4]arene, followed by hydrolysis the octaester to give the corresponding **1** or **2**. For a detailed procedure; see Ref. 3.

8 The aminated substrates were immersed in a THF solution (1×10^{-4} mol dm^{-3}) of **1** or **2** at 40 °C for 30 min. SAMs were obtained after rinsing with THF and drying at 80 °C for 30 min.

9 The value was estimated by π-A isotherm measurements of CRA-CMs incorporating azobenzene units according to Ref. 3b.

10 The aminated Au substrates were prepared by immersing cleaned Au substrates in a 1×10^{-3} mol dm^{-3} ethanolic solution of 2-aminoethanethiol in ethanol for 6 h at 25 °C.

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