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# Adsorption behaviors of poly(amido amine) dendrimers with an azacrown core and long alkyl chain spacers on solid substrates

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### Abstract

Adsorption behaviors of functional poly(amido amine) dendrimers with an azacrown core and long alkyl chain spacers were investigated on gold and self-assembled monolayer (SAM) by means of time course attenuated total reflection–surface enhanced infrared absorption and surface plasmon resonance spectroscopies. While 1.5th and 2.5th generation (G1.5 and G2.5) ester-terminated dendrimers were slightly adsorbed on all substrates examined, the adsorption of G2 amine-terminated dendrimer increased in the order dodecanethiol SAM < bare gold < 3-mercaptopropionic acid (MPA) SAM. The time course results also revealed that the G2 dendrimer displayed the steep increase of adsorption on the bare gold, followed by the slight progress of adsorption. G2 dendrimers adsorbed on MPA SAM involved their subsequent conformational rearrangement, while the adsorption equilibrium was quickly attained for G3 dendrimer on the MPA SAM. It was supported that G3 dendrimer was adsorbed with the perpendicularly extended structure on the MPA SAM substrate, and G2 dendrimer varied its conformation from the globular structure to the extended one perpendicular to the substrate. © 2005 Elsevier Inc. All rights reserved.

Keywords: Dendrimer; Poly(amido amine) dendrimer; Azacrown; Adsorption; Solid substrate; Self-assembled monolayer; 3-Mercaptopropionic acid;

Surface enhanced infrared absorption spectroscopy; Surface plasmon resonance spectroscopy

### 1. Introduction

Dendrimer is a unique polymer that has a monodisperse molecular weight, a highly symmetric structure and many terminal groups. These characters of a dendrimer are valuable on the applications like catalyst, sensor, drug delivery, and reaction matrix [1–6]. Many investigations have been developed for solutions and some were carried out for films [7,8]. The film morphology of dendrimer and/or dendron has been studied: poly(benzyl ether) dendron with a thiol focal point forms stripes of a self-assembled monolayer (SAM) on a gold substrate [9]. This dendron has a rigid structure that is attributed to aromatic moieties. Thus it is referred that such rigid dendrons and dendrimers can easily form ordered structures [10]. On the other hand, poly(amido

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amine) (PAMAM)-type dendrimers are flexible [11,12], and the films prepared from them have no ordered structure but present rather uniformly flat surface [13,14].

PAMAM dendrimer is useful for many applications due to its flexibility and cavernous interior, which control the conformation of PAMAM dendrimer in a film [15]. Moreover, the functional moieties can be introduced in a dendrimer in order to fabricate efficient catalysts and sensors. Meanwhile, azacrown derivatives selectively recognize some cations and molecules [16]. It is expected that an azacrown moiety in a dendrimer must be useful for molecular recognition, if the guest molecules could access to it. From these viewpoints, the synthesis and characterization have been carried out for a series of functional PAMAMtype dendrimers (aza-C6-PAMAM dendrimers, see Fig. 1) that have an azacrown core and long alkyl chain (hexyl) spacers [17]. While the ester-terminated aza-C6-PAMAM dendrimers formed homogeneous Langmuir films with face-

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Fig. 1. Molecular structures of G1.5-3 aza-C6-PAMAM dendrimers.

on configuration at the air–water interface, the dendrimers aggregated with silver nanoparticles by the aid of functional azacrown moiety on the aqueous suspension of silver nanoparticle as subphase [18].

To determine the layer formation and molecular ordering in films, surface spectroscopy such as surface plasmon resonance (SPR) sensing, reflectometry and surface enhanced infrared absorption and Raman spectroscopy have been developed [19–21]. On the surface enhanced spectroscopy, along with the merit that the vibration band intensity is enhanced, the surface selection rule works: perpendicular transition moment components of vibration modes are intensively observed [19]. Using SPR sensing and surface enhanced spectroscopy, the dendrimer layer thickness and molecular orientation in homogeneous and hybrid dendrimer films have been investigated [14]. The adsorption kinetics of dendrimers has also been analyzed on the basis of experimental results of adsorption isotherms from these methods [22].

In this study, the adsorption process of aza-C6-PAMAM dendrimers on solid substrates is examined by the surface enhanced infrared absorption spectroscopy (SEIRAS) and

SPR. Aza-C6-PAMAM dendrimers are more flexible than commercially available PAMAM dendrimer due to long spacers. On the occasion when controlling the conformation of dendrimers in films, it is expected that the position and approach of the functional azacrown core are variable as desired. The adsorption behavior of the dendrimers on gold substrate is compared to that on SAM substrate, which consists of reactive or nonreactive molecules. Moreover, the affinity of substrates with dendrimers possessing different terminal groups such as hydrophobic and hydrophilic ones is examined. The behaviors of dendrimers on the flat substrates are also discussed in comparison with that on silver nanoparticles, which was already investigated [18].

### 2. Experimental

Aza-C6-PAMAM dendrimers were synthesized as previously reported [17]. The generations of the dendrimers were 1.5 to 3 (G1.5–3, half generation is ester-terminated and full generation is amine-terminated). The other reagents were purchased from Aldrich Chemical Co. or Tokyo Kasei Co. and used without further purification.

Infrared (IR) absorption spectra were recorded with a Bio-Rad FTS 575C FT-IR spectrometer equipped with a liquid nitrogen-cooled MCT detector. Spectra were collected with 128 scans. Oily dendrimers were spread on KBr plates for measurements. Time course attenuated total reflection (ATR)-SEIRAS was measured by using a laboratory grade attachment [14]. Gold islands (10 nm thickness) were deposited at  $4 \times 10^{-4}$  Torr onto a silicon prism for SEIRAS. The gold island-deposited silicon prisms prepared were immediately used to the SAM formation: the prisms were immersed for 7200 s into an ethanol solution (1 mM) of 3-mercaptopropionic acid (MPA) or dodecanethiol, rinsed thoroughly with plentiful amounts of ethanol and then kept in vacuum until used. The SAM-coated silicon prism was attached to a Kretschmann-type flow cell system. The cell was first filled with methanol, and a background spectrum was collected as a reference. After methanol in the cell was replaced by a methanol solution (1 mM) of aza-C6-PAMAM dendrimer, time course ATR-SEIRAS measurement was carried out for 7200 s with 4 scans.

SPR examination was performed with a biosensor analytical system (Nippon Laser & Electronics Lab., 670 nm wavelength laser light). A flow cell was equipped on a goldevaporated glass substrate, which was coated with MPA SAM in the same way for ATR–SEIRAS. During the time course measurement, a methanol solution (1 mM) of aza-C6-PAMAM dendrimer was flowed on the substrate at a rate of 10 mm<sup>3</sup>/min. After 8200 s, the methanol solution was replaced to pure methanol at same flowing rate for the measurement involving rinse. Details of the measurement and the analysis are described elsewhere [14].

### 3. Results and discussion

### 3.1. IR absorption spectra of aza-C6-PAMAM dendrimers

IR absorption spectra of aza-C6-PAMAM dendrimers on KBr plates were drawn in Fig. 2, and the absorption bands were assigned, as listed in Table 1. Bands (amide A, B, I, II, III) of amide groups and bands ( $\nu_{as}$ (CH<sub>2</sub>),  $\nu_{s}$ (CH<sub>2</sub>),  $\delta$ (CH<sub>2</sub>),  $\omega$ (CH<sub>2</sub>)) of CH<sub>2</sub> groups were commonly observed in all generations of the dendrimers. The  $\nu_{as}$ (CH<sub>3</sub>) and  $\nu_{s}$ (CH<sub>3</sub>) bands of CH<sub>3</sub> groups in G1.5 and G2.5 were small shoulders of  $\nu_{as}$ (CH<sub>2</sub>) and  $\nu_{s}$ (CH<sub>2</sub>) bands, respectively. The  $\nu$ (C=O) and  $\nu$ (C–O–C) bands of terminal methyl ester groups in G1.5 and G2.5, and the bands ( $\nu$ (NH<sub>2</sub>),  $\delta$ (NH<sub>2</sub>),  $\omega$ (NH<sub>2</sub>)) of terminal amine groups in G3 were also clearly observed. However, the bands of NH<sub>2</sub> groups in G2 overlapped with amide bands.

Splitting in the  $v_{as}(CH_2)$  band of G1.5 and G2.5 means that the CH<sub>2</sub> groups took two different configurations, that is, *trans* (lower wavenumbers) and *gauche* (higher wavenumbers) [23]. On the other hand, the  $v_{as}(CH_2)$  band in G2 and G3 was single, and its position suggested the stretched trans configuration of the alkyl chains. This difference indicates that the flexibility of alkyl chains in the dendrimers varied between ester terminal dendrimers and amine terminal ones. Two amide I bands were observed for G1.5 and G2.5, different from G2 and G3. This means that different types of amide structures coexist in G1.5 and G2.5, corresponding to two configurations of alkyl chains.

## 3.2. Adsorption behavior of aza-C6-PAMAM dendrimers with various generations on different substrates

Time course ATR–SEIRAS of G2 and G2.5 aza-C6-PAMAM dendrimers adsorbed on various substrates are shown in Figs. 2 and 3. Intensities of amide I and II bands of G2 on the bare gold substrate increased for approximately 3600 s and saturated. However, the intensities of these bands on the dodecanethiol SAM were very weak or not observed, indicating less or no adsorption. On the other hand, on the MPA SAM, the intensities of amide I and II bands increased for 1800 s and then decreased. Moreover, the ratio between them changed (these phenomena are discussed later). The tendency of adsorption depending on substrate was different between G2 and G2.5. Band intensities of G2.5 in the region of  $\nu$ (C=O), amide I, amide II and  $\delta$ (CH<sub>2</sub>) vibration modes were very weak on three substrates.

It is revealed for G2 aza-C6-PAMAM dendrimer that intensities of IR absorption bands are in the order MPA SAM > bare gold > dodecanethiol SAM. That is, G2 aza-C6-PAMAM dendrimer adsorbs strongly to the MPA SAM, mildly to the gold substrate and scarcely to the dodecanethiol SAM. On the other hand, the adsorption of G2.5 aza-C6-PAMAM dendrimer is weak on all substrates used in this study.

The terminal amine groups of G2 aza-C6-PAMAM dendrimer are suggested to interact electrostatically or by hydrogen bonding with terminal carboxyl groups of the MPA SAM. It is known that adsorption behaviors of commercially available PAMAM dendrimers depend on the terminal groups of the dendrimers [24,25]. It might be expected that not only primary amine groups of a G2 dendrimer but also the tertiary amine groups of G2 and G2.5 dendrimers interact with the MPA SAM. Although the total number of tertiary amine groups of G2.5 aza-C6-PAMAM dendrimer is the same as the total number of primary and tertiary amine groups of G2 aza-C6-PAMAM dendrimer (24 per molecule), the adsorption of former dendrimer on MPA SAM was less than the latter. This indicates that the tertiary amine groups of dendrimers keep out of the interaction with MPA SAM. This means that the difference of terminal groups affects the adsorption behaviors, but the interior tertiary amine groups less contribute to the adsorption. The less efficiency of interior amine groups is supported from the reason that there is hydrogen bonding between amide groups within dendrimer, and such hydrogen bonding forms networks in the interior of dendrimer. The formation of such hydrogen bonding could



Fig. 2. Transmission IR absorption spectra (on KBr) and time course ATR-SEIRAS (on MPA SAM) of G1.5-3 aza-C6-PAMAM dendrimers.

be supported by the amide I bands at lower wavenumber positions (see Table 2). Moreover, the steric hindrance of terminal ester groups of G2.5 prevents the interior amine groups from interacting with the other dendrimers. The less effect of the interior structure is also confirmed by the less adsorption of G2 and G2.5 dendrimers onto the dodecanethiol SAM. The alkyl groups in these dendrimers did not interact with the hydrophobic dodecanethiol SAM.

Time course ATR–SEIRAS of G1.5–3 aza-C6-PAMAM dendrimers on MPA SAM are compared in Fig. 2. Main SEIRAS bands of G1.5, G2 and G3 aza-C6-PAMAM dendrimers on MPA SAM are listed in Table 2 and compared with those of G2 on bare gold. The intensities of  $\nu$ (C=O), amide I and  $\delta$ (CH<sub>2</sub>) bands of G1.5 at 1707, 1626 and

1453 cm<sup>-1</sup> are still weak but slightly stronger than those of G2.5. This result indicates that the interaction of G1.5 with the MPA SAM is stronger than that of G2.5. Since G1.5 is less branched and more flexible than G2.5, the steric hindrance of terminal groups is small, and the interaction of azacrown moiety with the carboxyl group of MPA may occur. This tendency is opposite to the adsorption behavior of same dendrimers with MPA-coated silver nanoparticle at the air–aqueous suspension interface [18]. The difference could be explained by the conformational difference of dendrimer molecules, since the hydrophobic terminal groups were oriented to the air phase, and the hydrophilic interior amine groups could interact with nanoparticles in the water phase. Such molecular ordering is preferable for the

Table 1 Assignments of IR absorption bands (in  $cm^{-1}$ ) of aza-C6-PAMAM dendrimers on KBr

Assignment	Ester terminal dendrimer		Amine terminal dendrimer	
	G1.5	G2.5	G2	G3
ν(NH <sub>2)</sub>			-	3345
Amide A, B	3276, shoulder	3306, -	3287, 3059	3289, 3051
$\nu_{as}(CH_3), \nu_s(CH_3)$	shoulder, 2854	shoulder, 2856		
$\nu_{as}(CH_2), \nu_s(CH_2)$	2951, 2934, 2821	2948, 2935, 2820	2928, 2856	2928, 2854
$\nu$ (ester C=O)	1740	1739		
Amide I	1670, 1654	1670, 1651	1647	1652
$\delta(\mathrm{NH}_2), \omega(\mathrm{NH}_2)$			_	1593, 1477
Amide II	1541	1545	1558	1568
$\delta(CH_2)$	1458, 1437	1449, 1437	1464, 1438	1463, 1440
$\omega(CH_2)$	1357	1357	1374	1375, 1358
Amide III (v(CN))	1255	1254	1310	1308, 1234
$v_{as}$ (ester C–O–C)	1200, 1174	1200, 1173		



Fig. 3. Time course ATR-SEIRAS of G2 and G2.5 aza-C6-PAMAM dendrimers adsorbed on gold and dodecanethiol SAM substrates.

higher generation dendrimer due to the high amphiphilicity. Meanwhile, G2.5 dendrimer molecules could take spherical conformation in methanol solution, indicating the less possibility for interior amines of dendrimer to contact with MPA SAM.

On the other hand, amide II,  $\omega(CH_2)$  and amide III bands of G3 at 1545, 1386, 1283 and 1253 cm<sup>-1</sup> were intensified from those of G2 and their intensities saturated at early stage of adsorption. Increasing adsorption of G3 may occur from the larger number of terminal amine groups, which concerned the interaction with MPA.

# 3.3. Adsorption/desorption process of amine-terminated G2 aza-C6-PAMAM dendrimer on different substrates

To confirm the adsorption of dendrimer on substrates, time course SPR angle shift was measured for G2 dendrimer on the bare gold and MPA SAM (Fig. 4). On both substrates,

Table 2 IR absorption bands (in  $\rm cm^{-1}$ ) of aza-C6-PAMAM dendrimers on substrates

Assignment	G1.5/MPA SAM	G2/gold	G2/MPA SAM	G3/MPA SAM
v(C=O)	1707			
Amide I	1626	1630	1650	1635
Amide II	-	1533	1558	1545
$\delta(CH_2)$	1453	1444	1471, 1457	_
$\omega(CH_2)$	-	1392	1385	1386
Amide III	-	1235	1289	1283, 1253
v(C=O) Amide I Amide II $\delta(CH_2)$ $\omega(CH_2)$ Amide III	1707 1626  1453 	1630 1533 1444 1392 1235	1650 1558 1471, 1457 1385 1289	1635 1545 - 1386 1283, 1253



Fig. 4. Time course differential SPR angle shift of G2 aza-C6-PAMAM dendrimer on gold and MPA SAM substrates.

the rapid angle shift almost saturated within 900 s and then gradually increased. After rinse, the angle shift decreased but did not recover the zero angle.

SPR angle shift depends on the dielectric constant and the thickness of adsorption layer according to the Fresnel theory [20]. After the adsorption (7200 s) and the rinse (1800 s), the dielectric constant and the thickness of the G2 dendrimer film were calculated by fitting the calculated SPR curve to the observed one on the basis of the standard Fresnel theory for the four-layer model (glass/gold/adsorbate/ methanol) [14]. During the calculation, the values from literature [14] were used for the dielectric constants of glass and gold (2.29 and 13.6 + 2.26i, respectively). The dielectric constant of methanol (1.769) and the layer thickness of gold (41-42 nm) were calculated from a SPR spectrum of the three-layer (glass/gold/methanol) system. The dielectric constant and the thickness of adsorbate, which were evaluated using the parameters described above, were listed in Table 3.

Considering that a size of the calculated G2 dendrimer molecule is approximately 3 nm for the uniformly extended conformation, the adsorption profile of G2 on the substrates can be illustrated as shown in Fig. 5. On the gold substrate, G2 dendrimers formed an adsorption layer, thickness of which corresponded to about 3 molecules. The thickness of the G2 layer increased 10% after the rinse, but simultaneously its dielectric constant decreased as getting closer to that of methanol, indicating the penetration of methanol in the G2 layer. On the MPA SAM, the thickness of the G2 layer is thicker than that on the gold. As estimated from the large decrease of the thickness and the slight decrease

Table 3 Dielectric constant and thickness of adsorbate on gold substrate and MPA SAM

Substrate	Rinsing	Dielectric constant	Thickness (nm)
Gold	before	1.823	10.0
	after	1.785	11.0
MPA SAM	before	1.804	15.5
	after	1.796	10.0



Fig. 5. Adsorption (before and after rinse) models of G2 dendrimer on gold and MPA SAM substrates. Globular structure and size of a G2 dendrimer molecule calculated by means of MM2 method (CS Chem3D Pro) are also included.

of the dielectric constant, some G2 molecules were removed by rinsing.

It is assumed that the long alkyl chain spacers in the G2 dendrimer played a significant role for forming the multimolecular accumulation in the adsorbate layers. Although the multilayer formation of amphiphilic dendrimers was already reported [14], PAMAM dendrimer with short spacer hardly showed the interaction and the multilayer formation [26]. In this study, the long alkyl chains could interact each other via hydrophobic interaction in methanol, and such interaction may change during the adsorption process.

## 3.4. Conformational changes of aza-C6-PAMAM dendrimers during the adsorption

The difference of the adsorption process on gold and MPA SAM substrates must first depend on the interaction between adsorbate and substrate: the G2 dendrimer with amine terminals interacts with MPA SAM more than gold. Such difference of the interaction may bring about the



Fig. 6. Adsorption time dependence of amide (I and II) band intensities on ATR–SEIRAS of G2 and G3 aza-C6-PAMAM dendrimers. ( $\blacksquare \square$ ) G2 on bare gold; ( $\bullet \bigcirc$ ) G2 on MPA SAM; ( $\blacktriangle \triangle$ ) G3 on MPA SAM. ( $\blacksquare \bullet \blacktriangle$ ) Amide I; ( $\square \bigcirc \triangle$ ) amide II.

conformational change of adsorbate during the adsorption, which can be followed by the time course ATR–SEIRAS.

The band intensities of amide I and II in ATR–SEIRAS are plotted in Fig. 6 as the time dependence on the adsorption process. On the gold substrate, the intensities of amide I

and II bands of G2 dendrimer increased and saturated. This behavior is similar to the time dependence of the SPR angle shift. Moreover, there is no apparent change on the intensity ratio of amide I and II bands. This indicates that the G2 adsorbs fast at the early stage and gradually at the later stage on the gold substrate without any conformational change. Similar phenomenon was reported for the adsorption of commercially available PAMAM dendrimer on MPA SAM [26] and explained by the two-step adsorption mechanism [27].

On the adsorption onto the MPA SAM, the amide I and II bands of G2 dendrimer were rapidly intensified within first 1800 s, but their intensities decreased after that (see Fig. 6). The increasing intensity of both amide I and II bands in the early stage corresponds to the increase in the amount of adsorbed G2 dendrimer, similar to the increase in SPR angle shift. It should be noted that the intensity ratio of amide I and II bands of the G2 was turned after 4500 s: amide I band is stronger than amide II band before the 4500 s adsorption, and their intensities inverted after that. This phenomenon implies a conformational change of the G2. The transition moments of amide I and II bands are almost perpendicular and parallel, respectively, to an amide C-N bond (see Fig. 7) [28]. Therefore, it is assumed from the selection rule [20,28] that the orientation of C–N bond in the amide group of dendrimer in the adsorbed layer changes perpendicular to



Fig. 7. Conformations of G1.5-3 aza-C6-PAMAM dendrimers adsorbed on substrates.

the substrate after the adsorption at the early stage. This supports the fact that the gradual increase in SPR angle shift after 1000 s indicates the conformational change as well as the increase of adsorbate. Then the dendrimer should vary from the uniformly extended conformation to the oriented one, which has a perpendicular molecular axis to the substrate. The conformational change of the G2 dendrimer is illustrated in Fig. 7.

On the adsorption of G3 on MPA SAM, the intensities of amide I and II bands reached constant after 300 s (see Fig. 6), indicating the rapid attainment of the adsorption equilibrium. It was also suggested that the G3 dendrimer adsorbed to the MPA SAM faster than the G2 dendrimer. Larger number of terminal amine groups (24 for G3, 12 for G2) might facilitate the interaction with MPA. Moreover, the absorbance of amide II was always much larger than that of amide I (see Fig. 6), the intensities of amide III (mainly  $\nu$ (C–N)) and  $\omega$ (CH<sub>2</sub>) bands increased, and that of  $\delta$ (CH<sub>2</sub>) band decreased (see Fig. 2). The transition dipole moments of amide III and  $\omega(CH_2)$  vibration modes are parallel to the direction of the amide C-N bond, and the moment of the  $\delta(CH_2)$  band is perpendicular to the alkyl chain axis. Then, as illustrated in Fig. 7, the conformation of G3 is continuously ordered perpendicular to the substrate, probably due to the large size of G3 and the strong interaction of terminal groups with MPA SAM.

The orientation of G2 and G3 described above is comparable to the case of G1.5 dendrimer on MPA SAM. As seen in Fig. 2, the intensities of amide I and  $\delta$ (CH<sub>2</sub>) bands of G1.5 increase but that of an amide II band does not. From the selection rule, it is assumed that G1.5 dendrimer is flattened on the MPA SAM, as illustrated in Fig. 7. The  $\nu$ (C=O) and amide I bands of G1.5 in adsorption films shifted from those of corresponding dendrimer on KBr plate, as appeared from the comparison in Tables 1 and 2. This suggests that these groups were bound via hydrogen bonding to the adjacent amide and/or azacrown groups and/or carboxyl group in the MPA SAM (see Fig. 7).

As discussed above, the chemical species of substrate and the generation of dendrimer could control the conformation of dendrimer molecules in the adsorption film. These results lead to the localization of functional group, azacrown core, in the dendrimer. The location of azacrown in a film should affect the efficiency of molecular recognition of this film. Therefore, the present study indicates the possibility preparing an adsorbed film that has exquisite molecular conformation.

#### 4. Conclusions

The adsorption behaviors of G1.5 to G3 aza-C6-PAMAM dendrimers onto various substrates (gold and SAMs of dodecanethiol or MPA) were examined by ATR–SEIRAS. Time dependency and intensity ratio of amide I–III and CH<sub>2</sub> bands clarified the interactions of dendrimers with substrates and the dendrimer structures in the adsorbed films. The adsorption of G2.5 dendrimer was very limited on all substrates. This suggests that the interior groups are hidden by terminal ester groups and not contributed to the adsorption. On the other hand, G1.5 dendrimer may interact with MPA SAM substrate through the interior amide groups and/or azacrown, and the molecular conformation is flat to the substrate. The lower generation is allowed the flat conformation.

Although the adsorption of G2 dendrimer on the dodecanethiol SAM was also very less, the G2 dendrimer indicated the significant adsorption on the bare gold substrate and MPA SAM. Because of the interaction with the carboxyl groups on MPA SAM, the G2 dendrimer was allowed to rearrange and varied its molecular structure from globule to oriented one. On the other hand, the terminal amine groups in the G3 dendrimer intensively interacted with the carboxyl groups on MPA SAM, and the dendrimer had perpendicular molecular axis to the substrate. Abundant terminal amine groups of G3 lead stronger interaction than the G2 dendrimer.

In spite of many investigations about the morphology of adsorbed dendrimer layers on the solid surfaces using microscopic and spectroscopic methods, the conformational change of the dendrimer molecules during the adsorption was not deeply discussed. This new knowledge would develop a better understanding about the adsorption behavior of dendrimers and be helpful to control the molecular conformation of dendrimer in the adsorbed film and to optimize the position of functional azacrown core for the molecular recognition.

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### References

- D.A. Tomalia, A.M. Naylor, W.A. Goddard III, Angew. Chem. Int. Ed. 29 (1990) 138;
- D.A. Tomalia, A.M. Naylor, W.A. Goddard III, Angew. Chem. 102 (1990) 119.
- [2] J.M.J. Fréchet, C.J. Hawker, in: G. Allen (Ed.), Comprehensive Polymer Science, 2nd suppl., Elsevier Science/Pergamon, Oxford, 1996.
- [3] G.R. Newkome, C.N. Moorefield, F. Vögtle, in: Dendric Molecules: Concepts, Synthesis, Perspectives, VCH, Weinheim, 1996.
- [4] O.A. Matthews, A.N. Shipway, J.F. Stoddart, Prog. Polym. Sci. 23 (1998) 1.
- [5] M. Fischer, F. Vögtle, Angew. Chem. Int. Ed. 38 (1999) 884.
- [6] R. Esfand, D.A. Tomalia, DDT 6 (2001) 427.
- [7] F. Zeng, S.C. Zimmerman, Chem. Rev. 97 (1997) 1681.
- [8] F. Vögtle, in: Dendrimers III, in: Topics in Current Chemistry, vol. 212, Springer-Verlag, Berlin, 2001.
- [9] L. Zhang, F. Huo, Z. Wang, L. Wu, X. Zhang, S. Höppener, L. Chi, H. Fuchs, Z. Zhao, L. Niu, S. Dong, Langmuir 16 (2000) 3813.

- [10] V. Percec, W.D. Cho, G. Ungar, D.J.P. Yeardley, Angew. Chem. Int. Ed. 39 (2000) 1597.
- [11] V. Chechik, R.M. Crooks, Langmuir 15 (1999) 6364.
- [12] T. Cagin, G. Wang, R. Martin, G. Zamanakos, N. Vaidehi, D.T. Mainz, W.A. Goddard III, Comp. Theor. Polym. Sci. 11 (2001) 345.
- [13] V.V. Tsukruk, F. Rinderspacher, V.N. Bliznyuk, Langmuir 13 (1997) 2171.
- [14] M. Ito, T. Imae, K. Aoi, K. Tsutsumiuchi, H. Noda, M. Okada, Langmuir 18 (2002) 9757.
- [15] L. Sun, R.M. Crooks, Langmuir 18 (2002) 8231.
- [16] C. Mertesdorf, T. Plesnivy, P.A. Suci, Langmuir 8 (1992) 2531.
- [17] O. Yemul, M. Ujihara, T. Imae, Trans. Mater. Res. Soc. Jpn. 29 (2004) 165.
- [18] M. Ujihara, J. Orbulescu, T. Imae, R.M. Leblanc, Langmuir 21 (2005) 6846.

- [19] M. Osawa, K. Yoshii, Appl. Spectrosc. 51 (1997) 512.
- [20] H.G. Tompkins, W.A. MacGahan, in: Spectroscopic Ellipsometry and Reflectometry, Wiley, New York, 1999.
- [21] T. Imae, in: Encyclopedia of Surface and Colloid Science, Dekker, New York, 2002, p. 3547.
- [22] H. Nagaoka, T. Imae, Trans. Mater. Res. Soc. Jpn. 26 (2001) 945.
- [23] D.A. Myrzakozha, T. Hasegawa, J. Nishijo, T. Imae, Y. Ozaki, Langmuir 15 (1999) 3601.
- [24] T. Imae, M. Ito, K. Aoi, K. Tsutsumiuchi, H. Noda, M. Okada, Colloids Surf. A 175 (2000) 225.
- [25] J. Ledesma-Garcia, J. Manriquez, S. Gutierrez-Granados, Electroanalysis 15 (2003) 659.
- [26] H. Nagaoka, T. Imae, Int. J. Non. Sci. Numer. Sim. 3 (2002) 223.
- [27] H. Nagaoka, T. Imae, J. Colloid Interface Sci. 264 (2003) 335.
- [28] R.V. Duevel, R.M. Corn, Anal. Chem. 64 (1992) 337.