

Interactions between Organized, Surface-Confined Monolayers and Vapor-Phase Probe Molecules. 12. Two New Methods for Surface-Immobilization and Functionalization of Chemically Sensitive Dendrimer Surfaces

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In this report we demonstrate two new methods for covalently linking dendrimers to surfaces. In the first method (method 1) a poly(iminopropane-1,3-diyl) dendrimer with 64 terminal-amine groups is first attached to a mixed mercaptoundecanoic acid (MUA)/mercaptopentane (MP) self-assembled monolayer (SAM), and then the unreacted terminal-amine groups of the dendrimer are converted to amide-linked functional groups by condensation with acid chlorides. The second method (method 2) involves bulk-phase coupling of suitable functional groups with the primary-amine-terminated dendrimer followed by reaction of the few unfunctionalized primary amines with the MUA component of the SAM to yield amide linkages. Five different dendrimer terminal groups are considered: primary amine, benzamide, 4-(trifluoromethyl)-benzamide, butanamide, and triphenylacetamide. Fourier transform IR external reflection spectroscopy, ellipsometry, variable takeoff angle X-ray photoelectron spectroscopy, and surface acoustic wave device-based gravimetry reveal that these two approaches result in very different types of dendrimer monolayers. When the dendrimers are prepared by method 2, their surface concentration is lower than when the functionalization is done after attachment. However, the density of surface functionalities on each dendrimer is higher when dendrimer modification is performed prior to surface attachment. When the benzamido-terminated dendrimer surfaces are dosed with a variety of volatile organic compounds (VOCs), we find that the surface prepared by method 2 is more sensitive and that there is enhanced selectivity for the VOCs having π electrons. This result is interpreted in terms of π -stacking interactions with the aromatic groups on the dendrimer surfaces.

Introduction

This report illustrates two new methods for attaching functionalized dendrimers (Chart 1) to Au surfaces using a self-assembled monolayer (SAM) adhesion layer.¹ As we have shown previously,² and expand upon here, dendrimer-modified surfaces^{3–7} possess some unique structural and chemical characteristics that make them excellent candidates for chemically sensitive interfaces.² Thus, there is a clear incentive to develop new tools for manipulating, functionalizing, and analyzing surface-confined dendrimers.

Here, we prepare surface-confined dendrimer interfaces using two distinct strategies (Chart 2). In the first method (method 1) the amine-terminated dendrimer is first attached to a mixed mercaptoundecanoic acid (MUA)/mercaptopentane (MP) SAM, and then the unreacted terminal-amine groups of the dendrimer are converted to amide-linked functional groups by condensation with acid chlorides. The second method (method 2) involves bulk-phase coupling of suitable functional groups with the

primary-amine-terminated dendrimer followed by reaction of the few unfunctionalized primary amines on each dendrimer with the MUA component of the SAM to yield amide linkages. These two approaches result in very different types of dendrimer monolayers. When the dendrimers are prepared by method 2, their surface concentration is lower than when the modification is done after attachment. However, the density of surface functionalities on each dendrimer is higher when the modification is performed prior to attachment.

Dendrimers are polymers prepared by repetitive branching from a central core (Chart 1).^{2,8–11} They have three distinct anatomical features: a core, repetitive branch units (dendrons), and terminal functional groups. Dendrimer size increases with generation number, and its molecular conformation evolves. At generation 0 or 1 (G0 or G1) most dendrimers have an expanded or "open" configuration, but as they grow in size, crowding of the surface functional groups causes the dendrimer to adopt a spherical or globular structure. Surface-confined dendrimers are highly versatile chemically sensitive interfaces for detecting volatile organic compounds (VOCs) for the following reasons. First, they are dense on the outside but somewhat hollow on the inside. This means that VOCs can sorb into the interior of the dendrimer and can be size selected by synthetically controlling the dimensions of the pores that result from packing of the outer-most branches of the dendrimer. Second, the chemical structure of both the exterior and interior of the dendrimer can be

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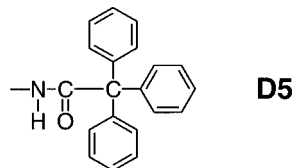
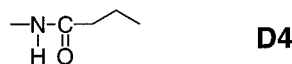
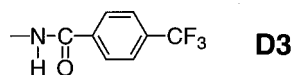
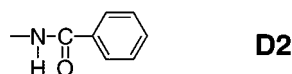
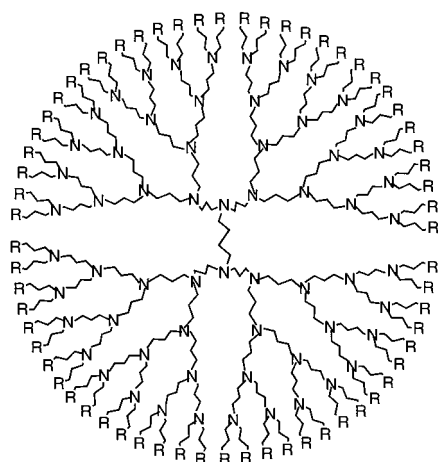
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Chart 1



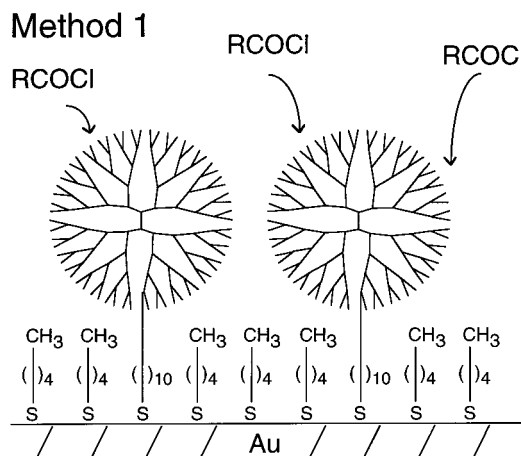
tailored for specific applications, which greatly enhances molecular specificity.²

Besides our own work, others have used a variety of noncovalent means for surface immobilization of dendrimers. For example, a dendrimer having electroactive ferrocene terminal groups has been electrochemically precipitated onto a Pt electrode.³ Dendrimers similar to those discussed here have been immobilized on glass and related material by spontaneous chemisorption.⁷ Layer-by-layer growth of dendrimers has been achieved via alternate complexation of the amine-terminated groups with Pt^{2+} .⁵ A similar approach was used to make thin films consisting of alternate layers of dendrimers having acid- and amine-terminal groups.⁶ Finally, Langmuir films of dendrimers have also been prepared.⁴

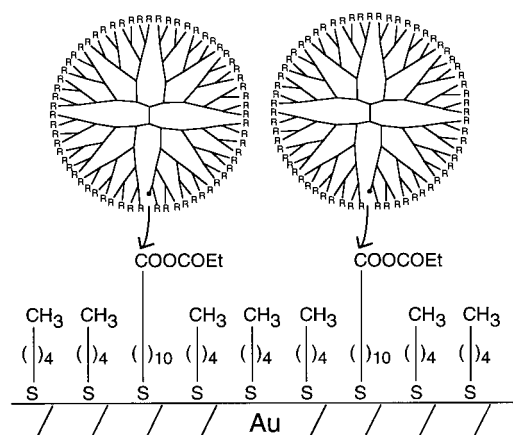
Experimental Section

Substrates. Au-coated substrates were prepared by electron-beam deposition of 100 Å of Ti followed by 2000 Å of Au onto Si(100) wafers. Au-coated SAW devices were prepared in the same manner on polished ST-cut quartz. Before each experiment all wafers and devices were cleaned in a low-energy Ar plasma cleaner at medium power for 1 min (Harrick Scientific Corp., New York, Model PDC-32G).¹² Mixed SAMs were prepared by immersing the Au-coated substrates in a 1 mM ethanol solution containing a 1:20 molar ratio of MUA/MP for 12 h.¹³ The

Chart 2



Method 2



substrates were then rinsed copiously with ethanol and water and then dried under flowing N_2 .

Chemicals. Fifth-generation amine-terminated poly(imino-propane-1,3-diyl) dendrimer, **D1** (sometimes referred to as 64-Cascade:1,4-diaminobutane[4]:(1-azabutylidene)⁶⁰:propylamine, or simply DAB(PA)₆₄, DSM Fine Chemicals, The Netherlands), was used as received. The radius of **D1** determined by small-angle neutron scattering is 1.39 nm (technical data supplied by the manufacturer). Benzoyl chloride (Aldrich 99%), 4-(trifluoromethyl)benzoyl chloride (Aldrich 97%), butyryl chloride (Aldrich 99+%), triphenylacetic acid (Aldrich 99%), thionyl chloride (Aldrich 99+%), ethyl chloroformate (Aldrich 97%), *n*-heptane (Aldrich 99+%), benzene (Aldrich 99.9%), carbon tetrachloride (Aldrich 99.9%), trichloroethylene (J. T. Baker 99.9%), and 1-butanol (Aldrich 99.8%) were also used as received.

Procedures. Dendrimers (**D2–D5**) were synthesized by the same general procedure. For example, in the case of **D3** 4-(trifluoromethyl)benzoyl chloride (557 mg, 2.68 mmol) was added dropwise to a dry 10 mL CH_2Cl_2 solution containing 300 mg (0.042 mmol) of DAB(PA)₆₄ and 0.1 mL of dry triethylamine under a N_2 atmosphere at room temperature. The mixed solution was stirred overnight. After solvent was removed, the residue was dissolved in CHCl_3 and washed with saturated aqueous solutions of Na_2CO_3 and NaCl. Drying with Na_2SO_4 followed by evaporation of the solvent yielded 628 mg (82%) of **D3**. $^1\text{H-NMR}$ (200 MHz) indicated that 90–98% of the amine groups of dendrimers **D2–D5** were functionalized by this procedure.

The mixed SAM substrate was soaked in a CH_2Cl_2 solution containing ethyl chloroformate and triethylamine for 1 h, followed by copious washing with CH_2Cl_2 . This procedure led to mixed anhydride activation of the MUA acid groups.² The substrates were transferred to a glass reaction vessel purged with N_2 , followed by addition of the coupling reactants: 10 mL of dry CH_2Cl_2 solutions containing 0.16×10^{-3} mmol of dendrimer and

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2 mg of triethylamine for the **D1** surface; 10 mL of dry CH_2Cl_2 solutions containing 1×10^{-3} mmol of dendrimers and 2 mg of triethylamine for the **D2–D5** surfaces. The solutions were stirred for 15 h. The substrates were removed from the solutions, washed with CH_2Cl_2 , ethanol, and H_2O , and then dried with flowing N_2 . For method 1, the **D1** surface was also soaked in a 10 mL CH_2Cl_2 solution containing 0.1 mmol of the appropriate acid–chloride derivative and 20 mg of triethylamine, for 15 h.

Characterization. Fourier transform infrared external reflection spectroscopy (FTIR-ERS) measurements were made using a Digilab FTS-40 spectrometer equipped with a Harrick Scientific Seagull reflection accessory and a liquid- N_2 -cooled MCT detector. All spectra were the sum of 256 individual scans using p-polarized light at an 84° angle of incidence with respect to the Au substrate.¹²

X-ray photoelectron spectroscopy (XPS) spectra were acquired using a Perkin-Elmer (PHI) Model 5500 spectrometer. XPS data acquisition employed a pass energy of 29.35 eV, a step increment of 0.125 eV, and a Mg anode power of 400 W. The F to N composition ratio was calculated from peak areas using appropriate sensitivity factors.

SAW device measurements were made at $25 \pm 0.5^\circ\text{C}$ using two (98-MHz) ST-cut quartz oscillators housed in a custom-built flow system.^{12,14} Modified SAW devices were dosed with VOCs diluted in N_2 to 25% of saturation (flow rate = 0.5 L/min). The change in SAW device frequency (Δf), due to the adsorption of vapor-phase molecules, is related to the mass loading per unit area (m_a) through the equation $\Delta f/f_0 = -\kappa c_m f_0 m_a$. Here, f_0 is the SAW resonance frequency (98 MHz), κ is the fraction of the distance between the centers of the transducers covered by the Au film (0.7), and c_m is the mass sensitivity coefficient of the device ($1.33 \text{ cm}^2/(\text{g}\cdot\text{Hz})$) for ST-cut quartz).¹⁴

Results and Discussion

We used mixed SAMs, consisting of a relatively low surface concentration of MUA diluted in MP, as adhesion layers for linking dendrimers to the Au surface: the acid terminus of the MUA component acts as a binding site for the dendrimers and MP as a lateral spacer. There are four reasons for choosing this approach. First, we have previously shown that attachment of dendrimers to single-component MUA monolayers² or direct sorption to Au¹⁵ results in distortion of the dendrimer shape. This new approach is more likely to result in surface-confined dendrimers that retain their bulk-phase conformation. Second, the surface concentration of dendrimers can in principle be controlled by varying the MUA/MP ratio. Third, reaction between the few available unfunctionalized amines (method 2) and MUA implies penetration of the acid group through the dendrimer functional groups; this action is enhanced if the acid extends above the organic surface (Chart 2). Fourth, a primarily low-energy, methylated surface resists contamination and interaction with the dendrimers. All of these effects are key to the use of dendrimer surfaces as chemically sensitive interfaces.

Figure 1 compares FTIR-ERS spectra of the pure MUA and mixed-MUA/MP SAMs. Consistent with previous results, the MUA-only SAM is dominated by asymmetric and symmetric CH_2 bands at 2922 and 2853 cm^{-1} , respectively,¹⁶ and carbonyl bands arising from monomeric and laterally hydrogen-bonded acid groups at 1738 and 1718 cm^{-1} , respectively.¹⁷ In the mixed SAM, the methylene bands, now arising from both MUA and MP, are still apparent in the high-energy part of the spectrum, but bands corresponding to the MP methyl groups

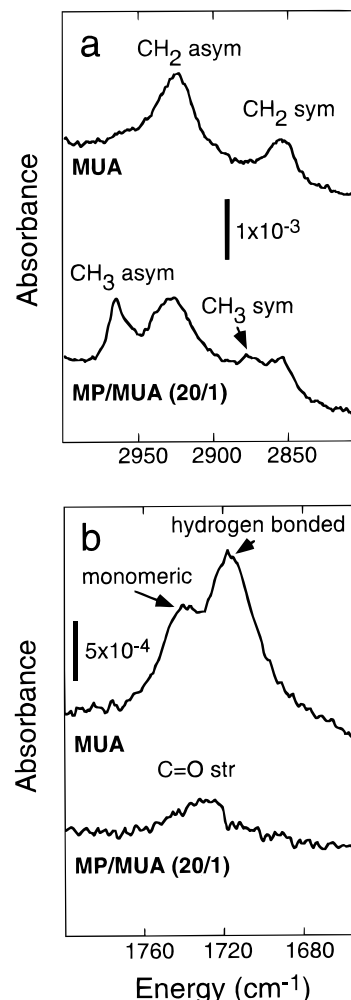


Figure 1. FTIR-ERS spectra of single-component mercapto-undecanoic acid (MUA) and two-component MUA/mercapto-pentane (MP) SAMs in the (a) high-energy (C–H stretching) and (b) low-energy (C=O stretching) regions.

are also present at 2965 and 2879 cm^{-1} , respectively.^{16,18} The intensity of the carbonyl band in the mixed SAM is greatly diminished compared to the MUA-only SAM indicating that it is a minor component of the mixed SAM. Additionally, the carbonyl peak in the mixed SAM is centered at 1731 cm^{-1} , which indicates that MUA is primarily configured in the monomeric form and thus accessible for chloroformate activation and subsequent reaction with the amine-terminated dendrimer.

Parts a and b of Figure 2 are spectra of a dendrimer surface prepared by method 1: The amine-terminated dendrimer (**D1** in Chart 1) is linked to the surface and then functionalized with benzoyl chloride to yield **D2**. Attachment of **D1** (Figure 2a) results in the appearance of the amide I and II bands at 1652 and 1561 cm^{-1} , respectively, which confirms that the dendrimer is linked to the SAM surface through covalent amide bonds. It is somewhat difficult to resolve the two amide bands completely because a peak around 1600 cm^{-1} , resulting from an NH_2 scissoring band associated with the dendrimer terminal groups, is also present in this region.¹⁸ Because the dendrimer is composed of propyleneimino branches, two kinds of methylene stretching bands arising from the dendrimer framework are present: the peaks at 2930 and 2857 cm^{-1} are typical of alkyl CH_2 stretching

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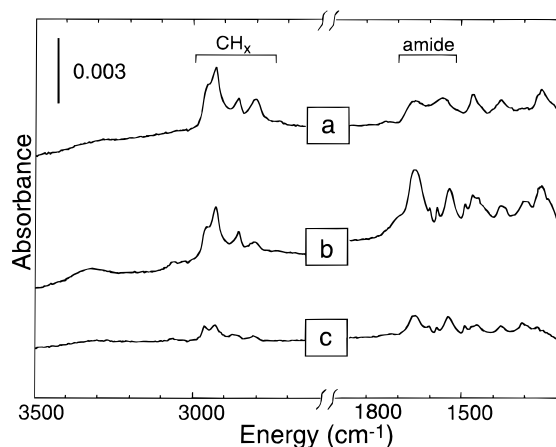


Figure 2. FTIR-ERS spectra of surface-confined dendrimers: (a) **D1**; (b) **D2** (method 1); (c) **D2** (method 2).

modes; the CH_2 peak at 2803 cm^{-1} is shifted because of the adjacent tertiary amine groups.¹⁸

Following dendrimer immobilization, the primary amines were reacted with benzoyl chloride to yield **D2**. This results in a dramatic increase in the amide band intensities (1650 and 1540 cm^{-1}) because of extensive amide coupling of the benzoyl functional groups, a decrease in the NH_2 scissoring band intensity, and new bands consistent with the presence of phenyl rings at 3065 , 1602 , 1578 , 1489 , and 1449 cm^{-1} (Figure 2b). Note that there is little change in the high-energy region of the spectrum indicating that SAM stability is compatible with the surface synthetic chemistry. Taken together, these results confirm dendrimer immobilization and on-surface functionalization.

Figure 2c shows an FTIR-ERS spectrum of a dendrimer surface prepared by direct immobilization (method 2) of prefunctionalized dendrimer **D2**. Amide bands are present at 1650 and 1544 cm^{-1} , but in this case it is not possible to distinguish between those arising from reaction between MUA and **D2** and those linking the functional groups to the dendrimer termini. To indirectly confirm covalent bonding of **D2** to the surface, therefore, we attempted to link **D2** to a MP-only SAM using the same chemistry that resulted in **D2** immobilization on the mixed SAM. Consistent with our contention of covalent binding to the mixed SAM, no IR signature of the dendrimers appeared on the MP-only SAM.

Comparison of the intensity of the IR bands in the hydrocarbon regions of parts b and c of Figure 2, which arise from the dendrimer skeleton, indicates that method 1 results in a significantly higher dendrimer surface concentration than method 2. This observation is supported by ellipsometric data: the thickness of the film corresponding to Figure 2b is 30 Å , while that of Figure 2c is only 20 Å . We speculate that the difference in the extent of dendrimer immobilization reflects the bulkiness associated with the benzoyl functionalities and the corresponding steric isolation suffered by the remaining amine groups. Note that in going from Figure 2c to Figure 2b, the bands in the amide region are not attenuated quite as much as the those in the hydrocarbon region. This suggests, and X-ray photoelectron spectroscopy (XPS) data discussed later confirm, that although method 2 results in a lower number density of dendrimers on the surface, individual dendrimers are more highly functionalized than when using method 1.

The FTIR-ERS spectra also show that after attaching the functionalized dendrimers, the amide bands at 1650 and 1544 cm^{-1} , which are influenced by inter- and intramolecular hydrogen bonding, are only slightly shifted

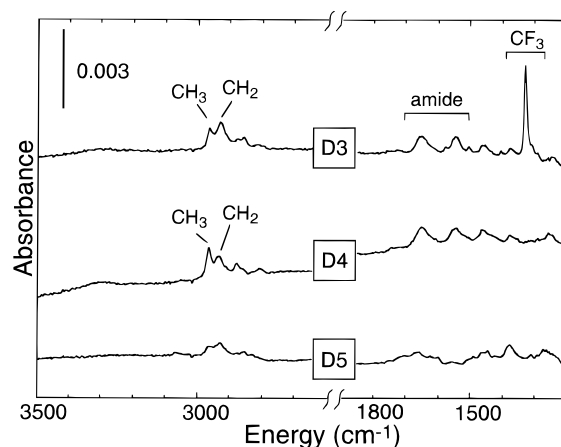


Figure 3. FTIR-ERS spectra of surface-confined dendrimers **D3**, **D4**, and **D5** prepared using method 2.

relative to the amide peaks at 1637 and 1541 cm^{-1} associated with **D2** in the bulk phase. This indicates that the amide bonds of surface-bound dendrimers are not strongly influenced by immobilization and thus remain strongly hydrogen bonded to one another.

To demonstrate the versatility of this approach for preparing dendrimer surfaces, we prepared surface-immobilized dendrimers **D3–D5** (Scheme 1) using method 2 (Figure 3). The spectrum of **D3** shows a characteristic, strong peak at 1333 cm^{-1} resulting from the C–F stretching mode of the 4-(trifluoromethyl)benzamido group. The dominance of this spectral feature suggests a high degree of dendrimer functionalization. The FTIR-ERS spectrum of the **D4** surface reflects an increase in the magnitude of CH_3 asymmetric stretch at 2965 cm^{-1} compared to the **D3** surface where the CH_3 bands arise only from the MP component of the mixed SAM. The IR spectrum of **D5** in the bulk phase shows the amide I peak shifts to significantly higher energy (1661 cm^{-1}) while the amide II peak shifts to lower energy (1500 cm^{-1}) compared with **D2–D4**. This indicates the amide groups of **D5** exist in the almost non-hydrogen-bonded state due to steric crowding by the massive triphenylacetamide group. This bulky group also hinders reaction between the activated acid groups in the SAM and buried primary amine groups on the dendrimer, and therefore the magnitude of the amide I and II bands is reduced compared to **D2–D4**.

Variable takeoff angle XPS reveals some interesting details about the chemical nature of the dendrimer surfaces prepared by the two routes. For this study we chose the 4-(trifluoromethyl)benzamido-modified dendrimer **D3**, because F has a high XPS sensitivity factor, and compared the atom ratio of F to N for dendrimer surfaces prepared by methods 1 and 2 using the peak areas of $\text{F}(s_1)$ at 688.4 eV and $\text{N}(s_1)$ around 400.2 eV (referenced to $\text{Au}(4f_{7/2})$ at 84.00 eV). Figure 4 indicates that the F/N ratio decreases substantially as the takeoff angle increases for the surface prepared by method 1, while it is almost constant for the data obtained using method 2. These results are consistent with an anisotropic distribution of F on the postfunctionalized surface, as illustrated schematically in Figure 4, and an isotropic distribution of F on the prefunctionalized surface. Certainly the latter result is anticipated since the dendrimer is modified prior to surface immobilization. Importantly, however, postfunctionalization apparently results in disproportionate fluorination of the top-most portion of the dendrimer surface, consistent with the higher dendrimer surface concentration established by the IR results for method 1, and correspondingly hindered access of the

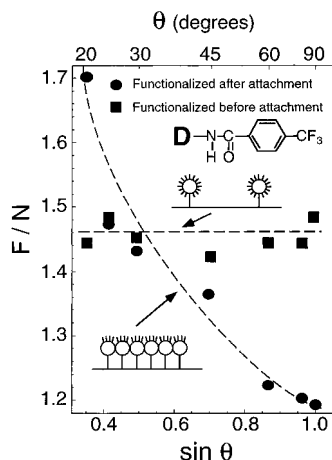


Figure 4. Variable takeoff angle XPS results comparing the composition ratio of F/N for **D3** prepared by method 1 (circles) and method 2 (squares).

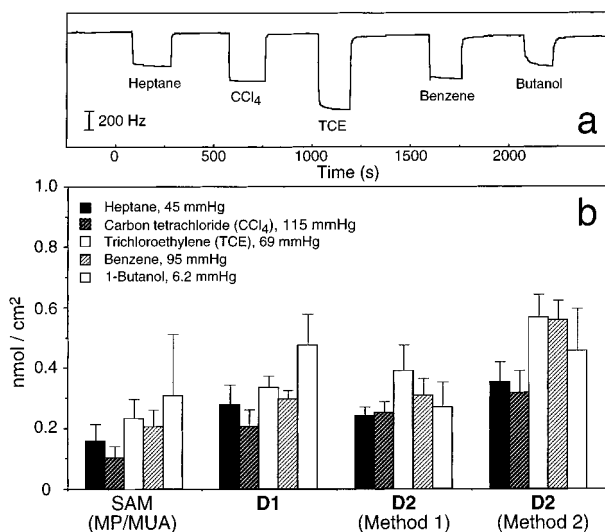


Figure 5. Mass loading results obtained by dosing SAW-device-confined dendrimer surfaces with five VOCs: (a) unprocessed data showing frequency change as a function of time for a **D2**-modified surface prepared according to method 2; (b) histograms showing VOC surface concentrations for three different dendrimer surfaces and a mixed SAM control surface. Error bars represent the standard deviation from the average results obtained from three independently prepared SAW devices for the SAM control surface, **D1** and **D2** (method 1), and seven independently prepared SAW devices for **D2** (method 2). All dosing experiments were performed using 25%-of-saturation VOC diluted in N_2 . The calculated vapor pressures at 25 °C for the VOCs are shown in the legend (see ref 12).

4-(trifluoromethyl)benzoyl chloride to the reactive amines on the dendrimer surface.

To better understand the chemical properties of the dendrimer layers and evaluate their potential as chemically sensitive interfaces, we dosed them with the five VOCs shown in the legend of Figure 5, and then measured the extent of sorption using SAW mass balances. Part a of Figure 5 shows the unprocessed SAW-device response of a **D2**-modified surface prepared by method 2 to each of the five VOCs (present at 25%-of-saturation vapor pressure). The important conclusion resulting from these data is that the dendrimer surfaces sorb and desorb the VOCs quickly and reversibly; for example, the average time required to desorb 90% of the adsorbed VOC mass is about 9 s. Such short times probably reflect the time constant of the dosing system rather than the actual sorption/desorption of the analyte from the dendrimer surface.

Part b of Figure 5 provides a compilation of the dosing data obtained from experiments like that shown in part a for all 5 VOCs on the mixed SAM surface (as a control experiment) and the three different dendrimer surfaces corresponding to those described earlier for Figure 2. The molecular weight bias for the different VOCs has been removed from these data (but not the data in part a) by presenting the results in terms of surface concentration (nmol/cm^2). The key result is that the benzamido-terminated dendrimer surface (**D2**) prepared by method 2 shows enhanced selectivity for trichloroethylene (TCE) and benzene, which are planar compounds containing π electrons, compared to either the **D1** surface or the **D2** surface prepared by method 1. The control experiment shown on the left side of Figure 5b confirms that the dendrimers, rather than just the mixed SAM surface, are enhancing binding of the π -electron-containing VOCs. This result is somewhat surprising since method 2 results in a much lower number density of surface-confined dendrimers than method 1. We interpret these data in terms of strong π -stacking interactions between the benzamido-terminated dendrimers and the two planar VOCs. Such interactions should be enhanced at dendrimer surfaces that are more highly functionalized with benzamido groups (method 2). This suggests that the more highly functionalized dendrimers provide better recognition cavities for planar VOCs and underscores the relationship between dendrimer conformation and surface-attachment protocol. Enhanced selectivity for π -electron-bearing VOCs is confirmed by comparing the 1-butanol and benzene dosing data for the **D1** and **D2** (method 2) surfaces. On the **D1** surface, the highest loading is observed for the alcohol, which not only has the lowest vapor pressure of the VOCs but should also interact most strongly with the **D1** amine-terminal groups via hydrogen bonding. In contrast TCE and benzene, which have much higher vapor pressures than 1-butanol, sorb to a lesser extent. On the **D2** (method 2) surface this trend reverses: the absolute magnitude of adsorption of the low vapor pressure alcohol remains essentially constant, but the extent of adsorption of the TCE and benzene nearly doubles compared to the **D1** surface.

Conclusions

In summary, we have prepared SAM/dendrimer bilayers using two different methods. FTIR-ERS and angle-resolved XPS indicate that the number and configuration of the functional groups are different for the two methods: prefunctionalization followed by immobilization leads to a high degree of dendrimer functionalization, but a relatively low surface density of dendrimers, while on-surface dendrimer functionalization leads to relatively high surface density of dendrimer, but a modest degree of dendrimer functionalization. Dosing experiments show that prefunctionalization (method 2) leads to a more effective receptor system for conjugated planar analytes presumably because of the higher density of functional groups.

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