Supporting Information

Tip-Loading, Force-Dependent Tunneling Behavior in Alkanethiol Self-Assembled Monolayers Studied Through Conducting Atomic Force Microscopy

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Experiment details

A ~5 mM solution of alkanethiol was prepared in ~10 mL anhydrous ethanol. All the chemicals were purchased from Sigma-Aldrich. The molecular deposition was done on Au surface (Au (250 nm)/Cr (3 nm)/glass) in solution for 1-2 days inside a nitrogen-filled glovebox with an oxygen level of less than 20 ppm. From AFM measurement, we confirmed the formation of ordered self-assembled monolayers within grain size of 50-200 nm in the Au substrates. This size would fully cover tip-molecules contact area. Alkanethiols of various molecular lengths, octanethiol ($CH_3(CH_2)_7SH$, denoted as C8, for the number of alkyl units), dodecanethiol ($CH_3(CH_2)_{11}SH$, C12), and hexadecanethiol ($CH_3(CH_2)_{15}SH$, C16) were used to form the active molecular components. Before use, each sample was rinsed with a few mL of ethanol and gently blown dry in a stream of N_2.

Experiments were performed using a commercially available AFM system (PSIA, XE-100 model) with conductive AFM tips that were made from a Au (20 nm)/Cr (20 nm) coating around conventional AFM tips (Typical force constant of the cantilever from manufacturer specifications is 0.03 N/m). Two terminal DC current-voltage (I(V)) measurements were performed using a semiconductor parameter analyzer (HP4145B). Voltages were applied to the CAFM tip while the Au substrate was grounded. All electrical measurements were carried out inside a covered AFM chamber in ambient through which nitrogen gas was being passed to minimize the formation of a contamination layer on SAM surface and to keep constant humidity (relative humidity 25-30%).

Typically, we repeated the measurements at least 5-10 times on various sample positions to obtain one data point and the statistical error bar. We exclude I(V) data that exhibit low bias junction resistance of less than the resistance of a single conductance channel h/e^2 = 25.8 kΩ, which infers the presence of metallic short through the molecular layers and the junction resistance of more than several hundreds of GΩ, which infers electrical open due to a poor CAFM tip-molecules contact. When the CAFM I(V) measurements frequently produced an electric open or a short, we changed the CAFM tips or sample positions.

Estimating Contact Radius, Contact Separation, and Tilt Angle

The Johnson-Kendall-Roberts (JKR) contact model[S1] was used to evaluate the contact geometry in CAFM method.[S2] The JKR contact model considers the interfacial adhesion force which can be important at relatively small loads,[S1] and the model reflects the importance of interactions between the tip and the SAMs. According to the Johnson-Kendall-Roberts (JKR) contact model, the radius a of the junction area under the AFM tip contact is expressed by[S1]

$$\begin{aligned} a^3 &= (R/K)P_n \\ &= (R/K)\{P + 3\Gamma\pi R + (6\Gamma\pi RP + (3\Gamma\pi R)^2)^{1/2}\} \end{aligned} \quad ((S1)$$

where R is the radius of the AFM tip end, determined as ~35 nm by means of field emission scanning electron microscope (FE-SEM) images (a representative FE-SEM image of Au-coated tip is displayed in Figure S1.) and $K = (4/3)\left[(1-\nu_1^2)/E_1 + (1-\nu_2^2)/E_2\right]^{-1}$ where E_1, ν_1, and E_2, ν_2 are Young's modulus and Poisson's ratio of the sample and the Au-coated tip, respectively. Appropriate E_1, ν_1, E_2, and ν_2 are not available, but assuming $E_1 \approx 10$ GPa,[S2,S3] $E_2 \approx 69$ GPa,[S4] and $\nu_1 \approx \nu_2 \approx 0.33$[S5] compared to similar materials and

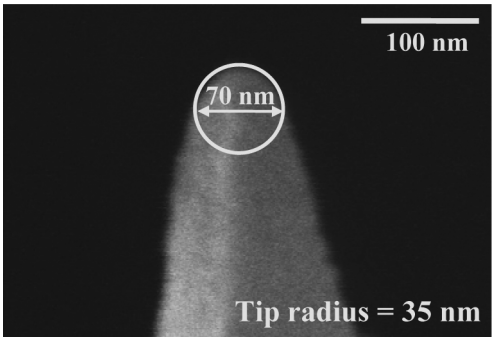

Figure S1. A field emission scanning electron microscope image of a Au-coated AFM tip.

Table S1. Contact radius and net force P_n of the junction contact areas calculated according to the JKR contact model (Eq. (S1)) for different length alkanethiols (C8, C12, and C16) at given tip-loading forces

	C8		C12		C16	
Tip-loading force (nN)	Net force (nN)	Contact radius (nm)	Net force (nN)	Contact radius (nm)	Net force (nN)	Contact radius (nm)
1	45.2	4.95	49.8	5.12	55.9	5.32
2	47.1	5.02	51.9	5.19	57.9	5.38
5	52.7	5.22	57.6	5.37	63.6	5.55
10	61.6	5.49	66.5	5.64	72.6	5.81
15	69.9	5.73	75.1	5.87	71.2	6.02
20	78.1	5.95	83.2	6.07	89.5	6.22
25	85.9	6.14	91.1	6.26	97.6	6.41
30	93.6	6.32	98.9	6.43	105	6.57

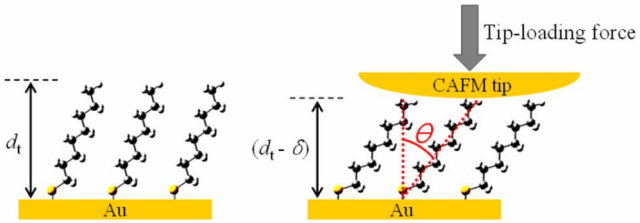

Figure S2. Schematics illustrating the geometry of molecules tilted by the tip-loading force.

structures, K can be calculated to be ~13 GPa. P_n is the net force, which is the sum of the applied loading force P and terms due to the adhesion force. $\Gamma = 2P_c/3\pi R$ is the adhesion energy per unit area related to the adhesion force P_c which can be obtained from a force-distance characterization. We obtained typical force-distance curves from which adhesion forces (P_c) of C8, C12, and C16 SAMs on Au substrate were determined to be 10.8 nN, 12 nN and 13.5 nN, respectively. Calculation results are listed in Table S1.

The contact separation ($(d_t - \delta)$ in Figure S2) is shortened when the tip makes contact with alkanethiol SAMs by the tip-loading force. The JKR contact model predicts the reduced distance δ as the following form.[S1,S6]

$$\delta = \frac{a^2}{R} - \sqrt{\frac{8\pi\Gamma a}{3K}} \qquad \text{(S2)}$$

We used each radius value of the contact junctions listed in Table S1. The average film thickness d_t of alkanethiol SAMs without tip contact was determined by ellipsometric measurements. The average film thickness d_t was estimated to be 1.15 nm, 1.60 nm, and 1.98 nm for C8, C12, and C16 SAMs, respectively. These thicknesses correspond to a molecular tilt of ~30° with respect to the Au substrate normal, as also observed in well-ordered alkanethiol SAMs on Au(111).[S7] The tilt angle θ of molecules under the tip contact can be geometrically calculated as $\cos^{-1}[(d_t - \delta)/d_m]$, as shown in Figure S3 where the molecular lengths d_m are 13.3, 18.2, and 23.2 A for the C8, C12, and C16 alkanethiols, respectively, (each molecular length was determined by adding an Au-thiol bonding length to the length of molecule).[S8]

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