Supporting Information

Thermal Curing of Self-Assembled Monolayer at the Nanoscale

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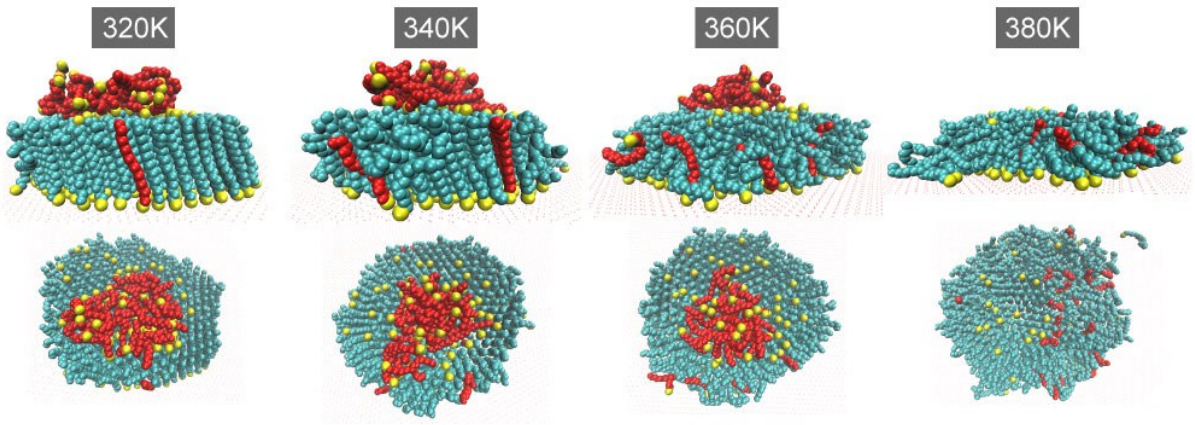

Fig. S1 Adsorption of molecules piled on top of the SAM island in the thermal annealing. Representative MD snapshots at 320, 340, 360, and 380 K are shown. The side and top views at each temperature are shown in the top and bottom rows, respectively. The unbound molecules piled on top of the SAM island at 300 K appear in red. At 320 K, only one molecule was found hopping down to the surface. At 340 K, four more molecules hopped down and only one adsorbed via the push-down pathway. At 360 K, four more molecules hopped down. At 380 K, five molecules adsorbed by following the hop-down path. The remaining 17 molecules followed the push-down pathway to achieve adsorption.

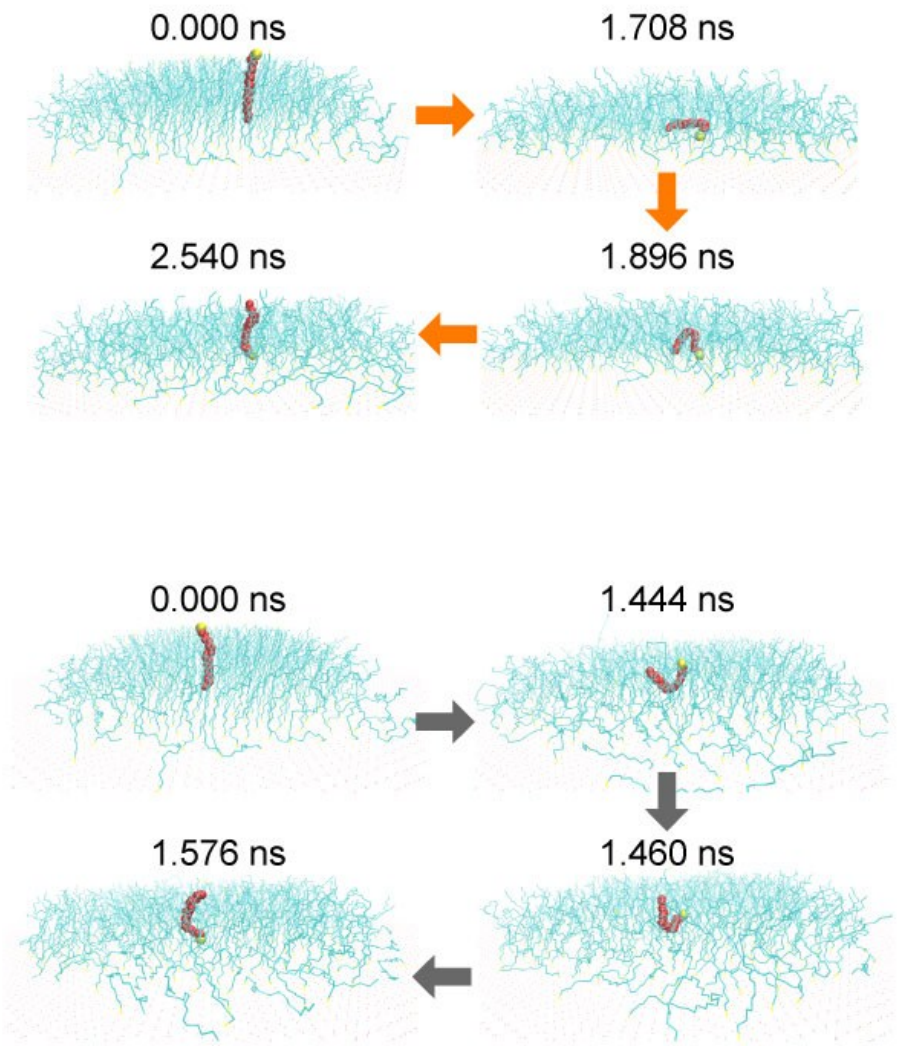

Fig. S2 Flipping of an inverted molecule at 400 K. An inverted molecule flipped by moving its sulfur atom down and methyl tail group up either sequentially (top) or simultaneously (bottom). In the sequential flip pathway (top), the sulfur atom of an inverted molecule penetrates down without moving its methyl tail group. After the sulfur atom adsorbs, the methyl tail group moves up to yield an upright molecule. In the simultaneous flip pathway (bottom), the sulfur atom of an inverted molecule lowers while raising its methyl tail group at the same time.

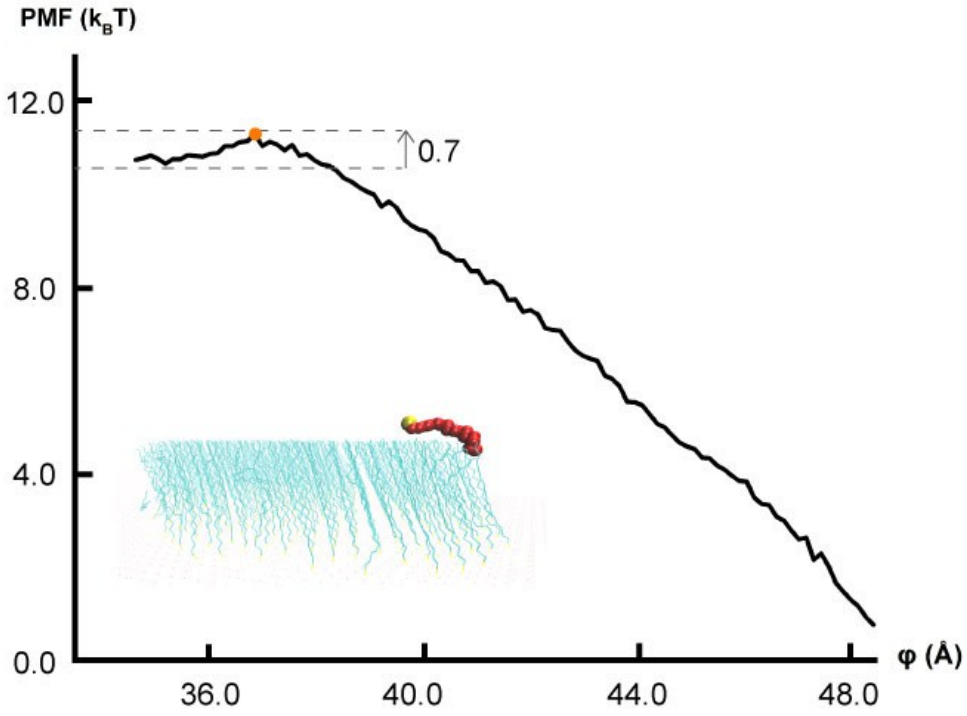

Fig. S3 Potential of mean force (PMF) profile for the adsorption of an ODT molecule via the hop-down pathway. Unlike the PMF profile shown in Fig. 4, the free energy profile above is obtained by removing the pile of molecules on top of the SAM island except the adsorbing molecule (in red). The free energy barrier, 0.7 k_BT in height, is an analog of the Ehrlich-Schwoebel barrier in the epitaxial growth of a metallic film. Also depicted is the configuration of the transition state.

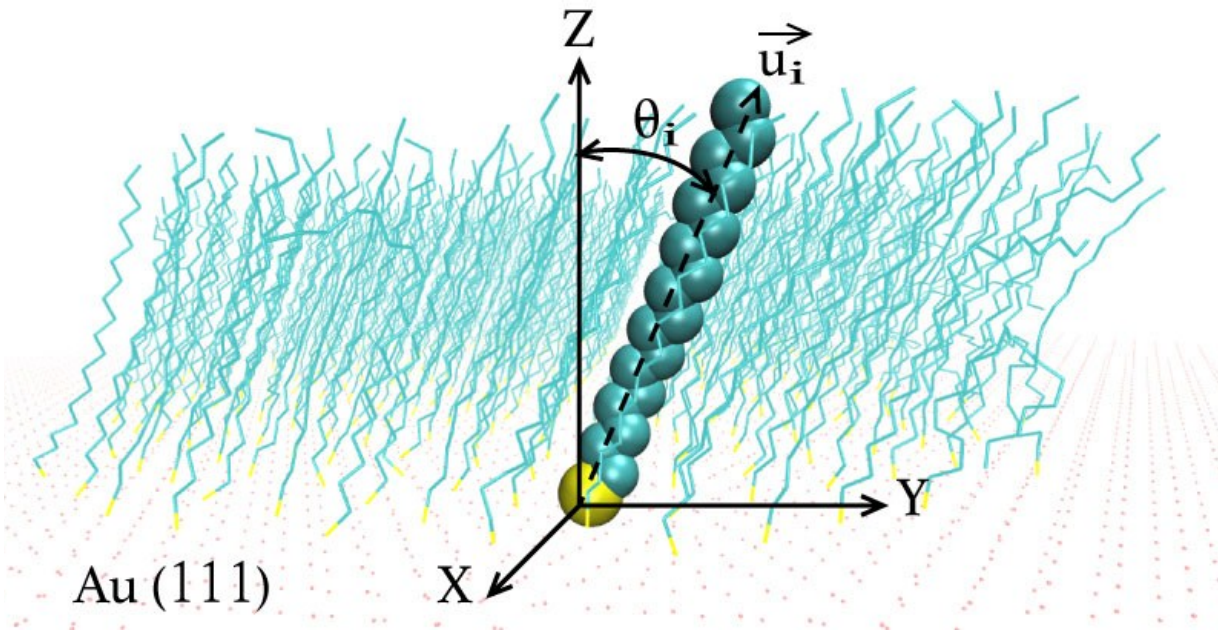

Fig. S4 Orientation of an ODT molecule adsorbed on the gold (111) surface. Highlighted is the *i*th molecule (out of 346 molecules) with all trans conformations. The tilt direction vector, $\vec{u}_i$, was defined by selecting CH_3 or CH_2 groups with odd (1–17) numbers of intervening CH_2 groups between them and the sulfur atom. The unit vector, $\vec{u}_i$, was defined as the average of the vectors from the sulfur atom to these selected groups. The tilt angle θ_i is the polar angle of $\vec{u}_i$ measured from the surface normal (Z direction).

Table S1 Structural parameters of the present SAM island after completion of thermal annealing. Listed are the average values of the sulfur-sulfur distance, d_{ss}, tilt angle of alkyl chains, θ, percentage of trans conformations, % trans, and orientational order parameter of alkyl chains, O_u. The corresponding values from the MD simulation of the bulk SAM without defects are listed for comparison. Also listed, in the third and fourth rows, are the results for the SAM islands annealed two and four times faster than in the present simulation, respectively. Decreasing the annealing rate enhances the quality of the SAM island, as manifested in the values of % trans and O_u.

	d_{ss}	θ	% trans	O_u
Present SAM island	4.97 Å	26.1º	97.1%	0.92
Bulk SAM without defects	4.99 Å	29.0º	99.0%	0.98
SAM island annealed 2x faster	5.00 Å	26.4º	96.3%	0.88
SAM island annealed 4x faster	4.99 Å	26.0º	95.1%	0.78