

Electronic Supporting Information

Dynamics and Molecular Interactions of Single-stranded DNA in Nucleic Acid Biosensors with Varied Surface Properties

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Additional Simulation Details and Discussion

The size of the SAM slab was 125 x 135. This size was chosen such that probes could lean significantly or adsorb to the SAM without entering the neighboring periodic cell. This provided more than enough space to ensure no correlation between periodic images of the probe. The SAM and gold surface were not separated from their periodic images in order to mimic a larger 2D surface. This design did not introduce any artifacts that would affect probe or target ssDNA behavior. Minor edge effects that may have affected movement of SAM molecules in the vicinity were circumvented by intentionally leaving out of our calculations any molecules within five rows of the edges. We constructed the water boxes for our systems such that the water ended exactly at the edges of the SAM. To avoid influence from the periodic images above and below, probe simulations had 20 Å of water above the probe tip and 15 Å below the gold substrate. Target simulations had 40 Å of water above the DNA and 10 Å below the gold substrate.

Salt concentrations ranged from approximately 0.010-0.020 M for the OH- and CH₃-SAM systems, 0.167 to 0.340 for the NH-SAM systems, and 0.516 to 1.09 M with the COO-SAM systems. Typical experimental salt concentrations for use of these biosensors are approximately 1 M, and human biological Na⁺ and Cl⁻ concentrations are normally 0.100-0.200 M. Our results indicate that salt concentration undoubtedly has an effect on DNA behavior, however a detailed analysis of this variable was beyond the intended scope of this work.

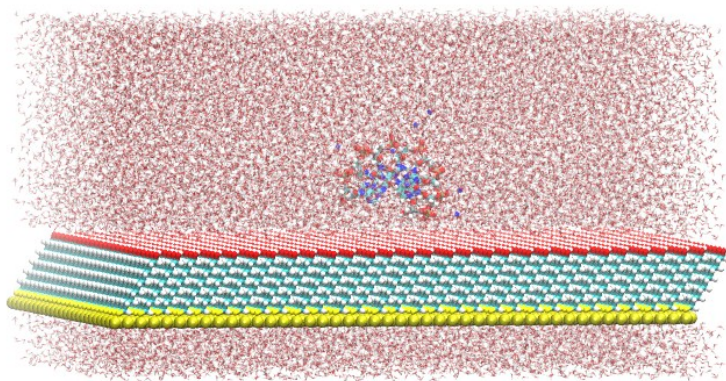
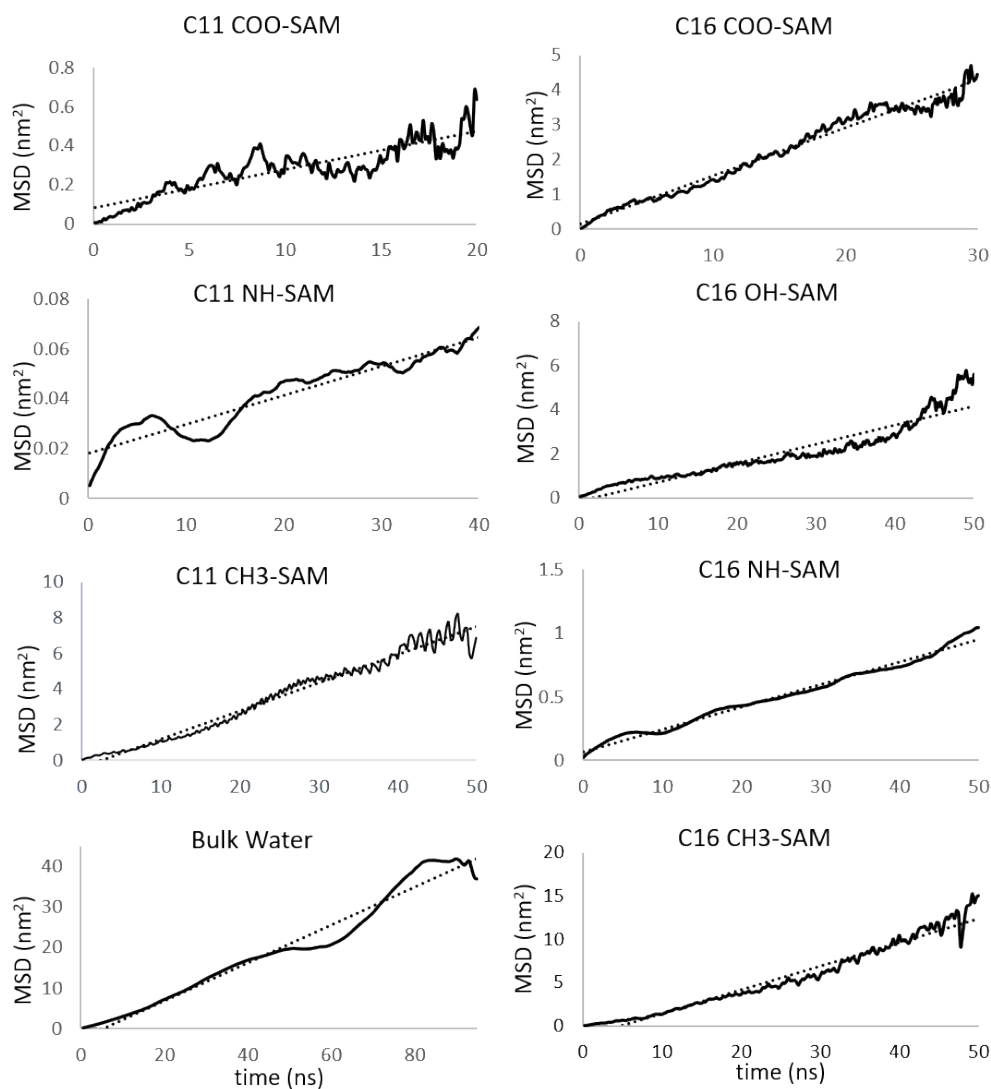


Figure S1. ssDNA above the OH-SAM as an example of the starting structure for a 5 Å-starting distance ssDNA target simulation. Water box is shown as transparent molecules. All simulations had a similar set-up, with water both above the SAM and below the gold. Water boxes were constructed in VMD and ended exactly at the edges of the SAM.



Diffusion Coefficient ($\times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$)								
10-ns period	C11 COO	C16 COO	C16 OH	C11 NH	C16 NH	C11 CH3	C16 CH3	Bulk Water
1	1.09	3.58	3.71	0.314	4.70	2.87	4.10	5.46
2	1.54	5.36	2.83	0.488	6.31	4.74	7.34	7.77
3	-	2.72	1.93	0.139	3.37	6.68	6.74	3.02
4	-	-	3.62	0.279	3.75	3.72	11.78	13.9
Overall	0.914	4.28	3.57	0.209	5.4	4.94	8.54	7.51
SD	0.225	1.10	0.720	0.120	1.13	1.42	2.50	4.04

Figure S2. Mean square displacement (MSD) over time for all simulations from which a diffusion coefficient was reported, and the diffusion coefficients from consecutive 10-ns blocks of each simulation. 1 is the first 10 ns of simulation, 2 is the second, as so on. Figure shows data from just one of the two runs for each system. Surface diffusion data were recorded only over periods of steady surface adsorption of ssDNA and not necessarily the entire simulation period.

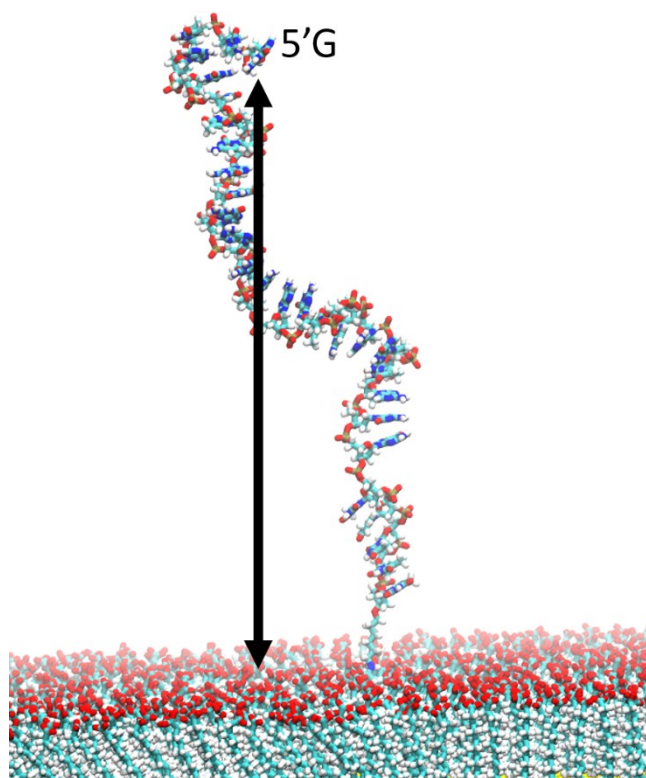


Figure S3. Graphical representation of the probe tip-SAM distance measurements. We calculated the minimum distance between any atom in the guanine at the 5' end of the probe and any atom in the SAM. The probe tip is not necessarily always the highest point of the probe above the SAM, but often it is, or is at least very close to being so. It was possible that the bottom or middle bases of the probe would adsorb to a surface while the tip remains several tens of Å above a surface, yielding misleading results about a probes elevation. However, after careful observation of the trajectories, we determined that this was never the case, and that the probe was never partially adsorbed and never adsorbed then desorbed. Thus, we can say that the probe tip to SAM distance is a good indication of the overall height of a probe above the surface.

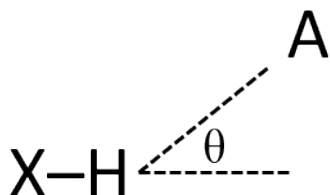


Figure S4. Depiction of the HB criteria used in this study. H is the hydrogen on the donor, and A is a lone-pair-containing oxygen or nitrogen on the acceptor. The distance between H and A must be less than 3.5 Å and θ must be less than 30° for a HB to be formed.

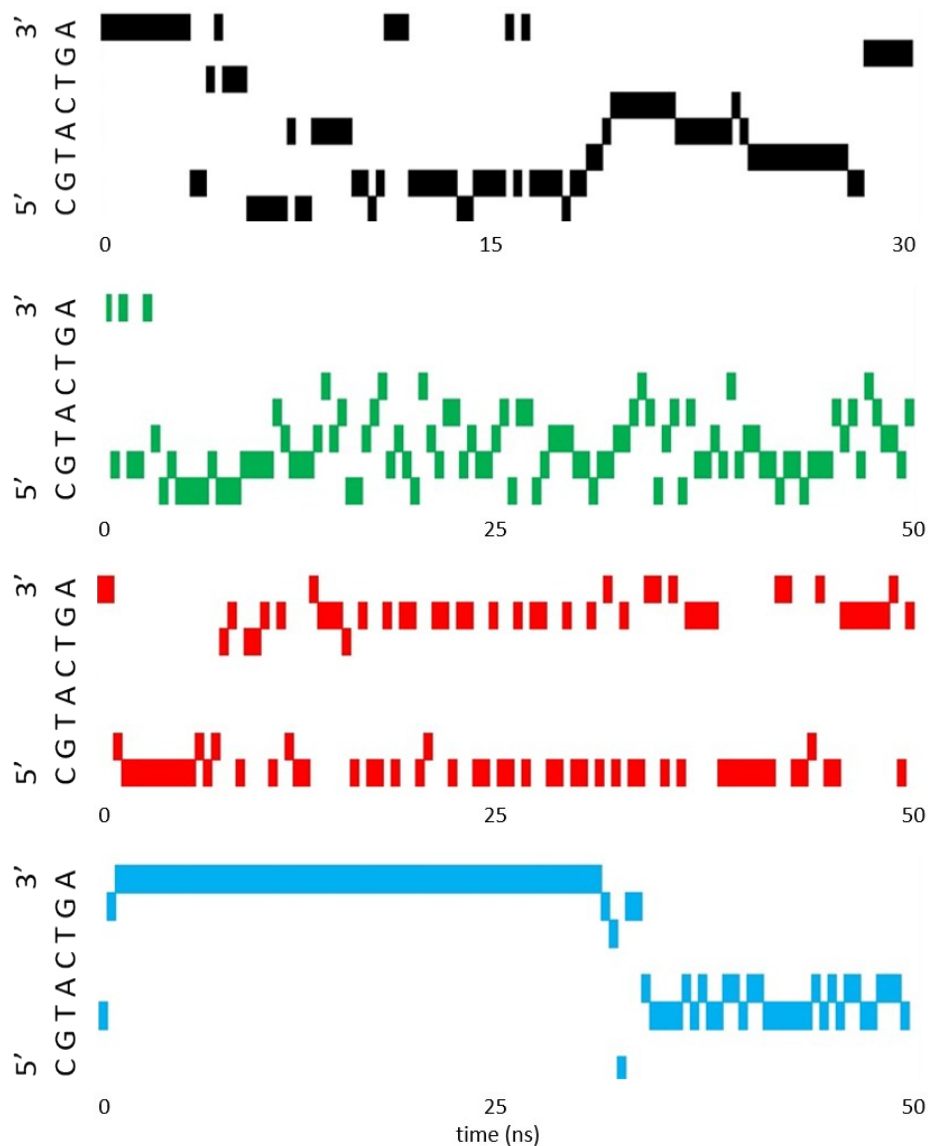


Figure S5. Contact map of 8-base ssDNA on the C16 length of the COO⁻ (black), OH⁻ (green), NH⁻ (red), and CH₃-SAM (blue). Highlighted box indicates the nucleotide closest to the surface at a particular time. Measurements were taken over the period in which ssDNA was adsorbed to the respective surfaces.

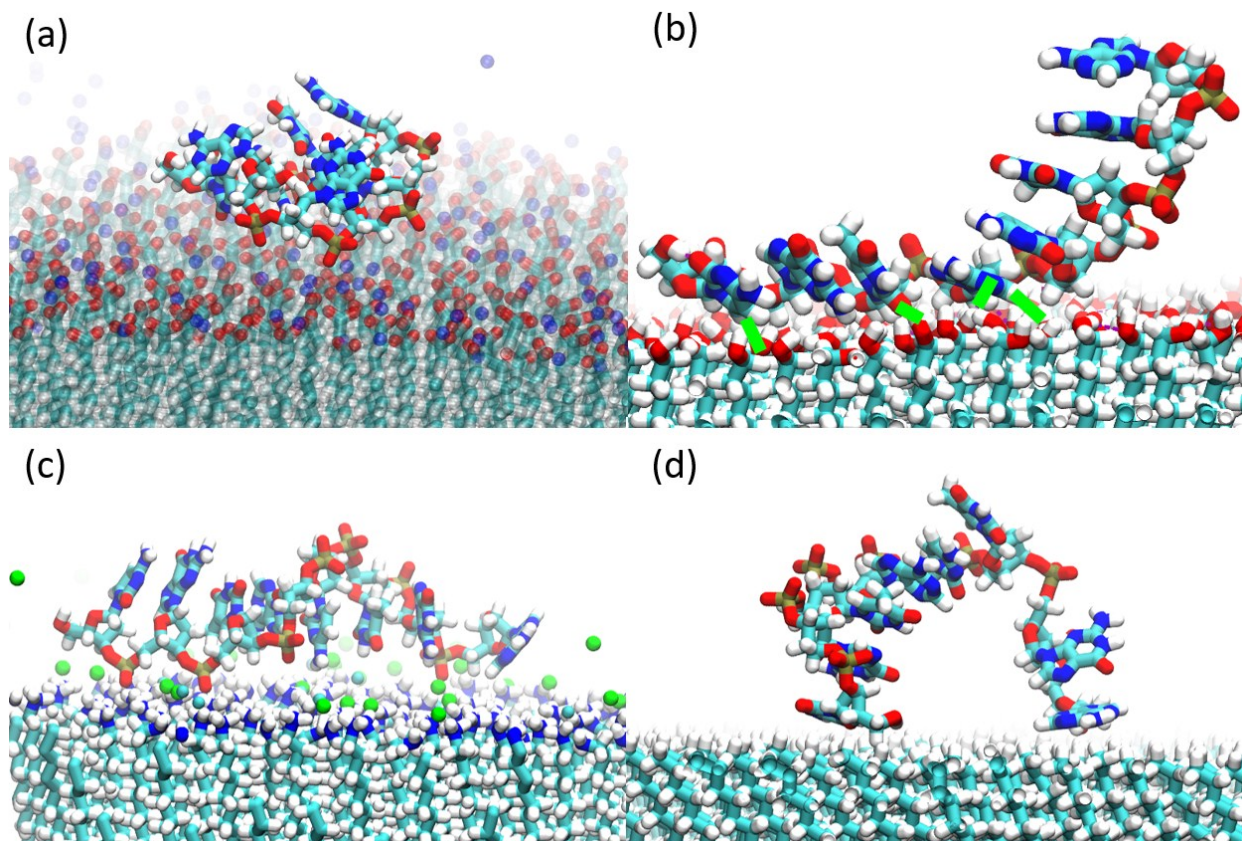


Figure S6. Representative conformations of adsorbed ssDNA on a) the C16 COO-SAM (blue spheres are Na⁺ ions), b) the C16 OH-SAM (bright green lines in indicate DNA-SAM HBs), c) the C11 NH-SAM (green spheres are Cl⁻ ions), and d) the C11 CH₃-SAM.

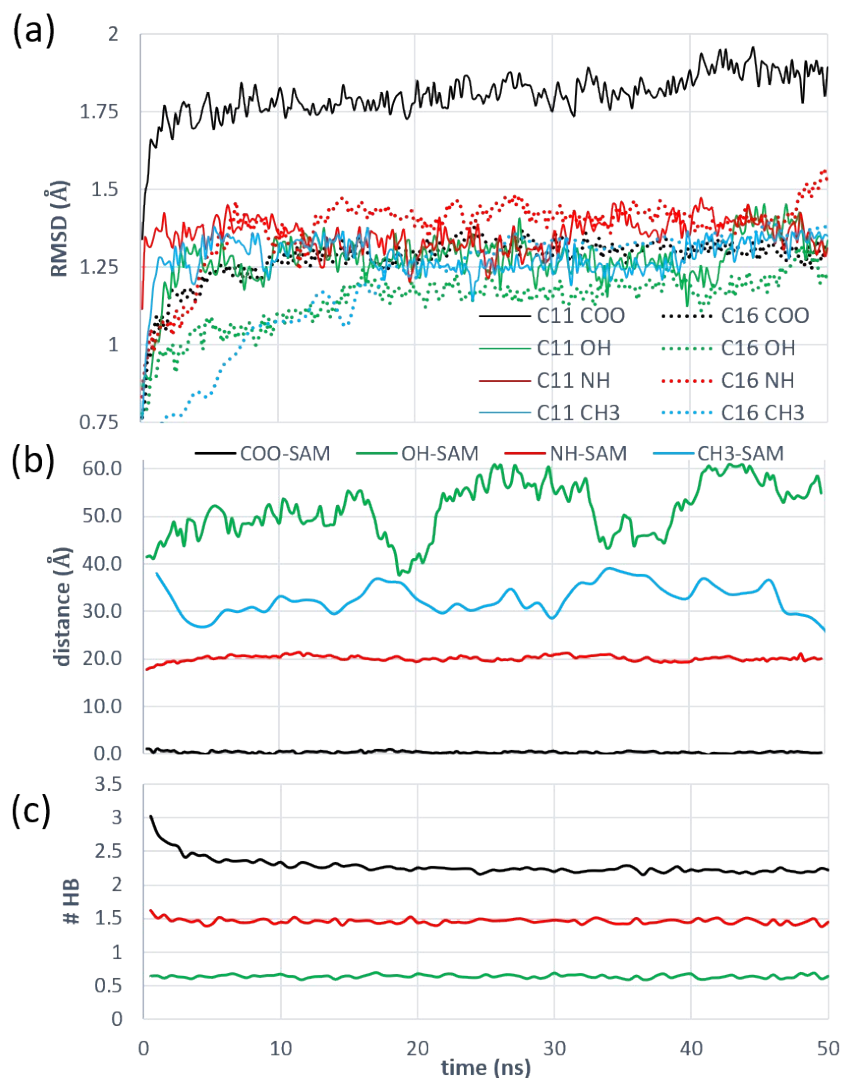


Figure S7. a) Root-mean-square deviations of all atoms (including hydrogen) for a set of 40 molecules in each of the different SAMs used, b) average distance of ions above the SAMs. COO is just visible above the x-axis because of strong adsorption, and OH and CH3 fluctuate because the number of ions (7) was very low compared to NH and COO (hundreds), and c) number of water-SAM hydrogen bonds per tail group for the C16 length of each SAM. COO- and NH-SAMs show a slight drop-off in the beginning as ions settle onto the surface and displace waters.

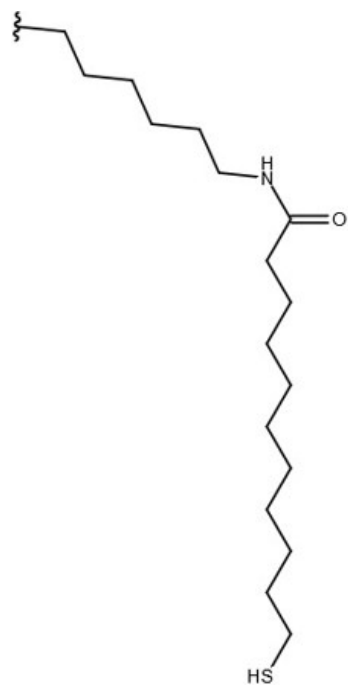


Figure S8. The linker molecule which attaches to the 3' end of the ssDNA probe and bonds to the gold substrate at the other via the thiol group. The same linker was used in all probe simulations.