Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Computational and Experimental Approach to Understanding the Structural Interplay of Self-assembled End-terminated Alkanethiolates on Gold Surfaces

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Figure S1: Free energy obtained from the AIMD simulation of model M8/C11TH along with four different configurations by including vdW dispersion correction optB86b functional in VASP.

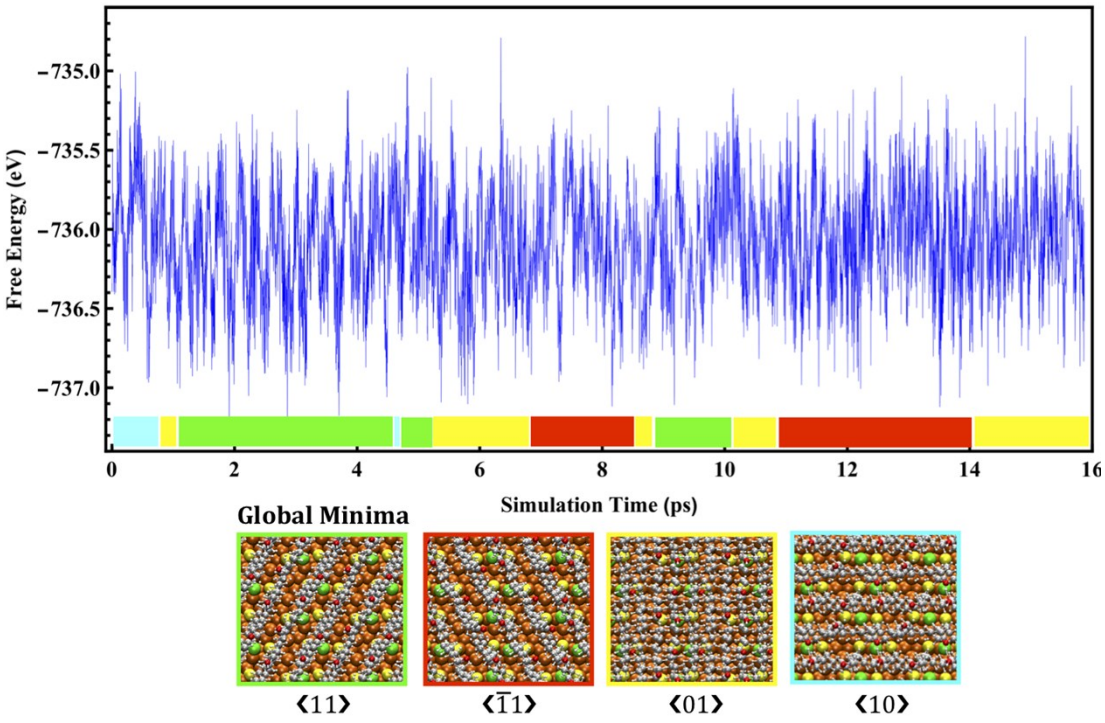

Figure S2: DFT optimized without simulated annealing different atomistic models of Au/ C11TH interface by using vdW density functional. Top row: top view *xy* plane and bottom row: side view *xz* and *yz* plane. Blue lines indicate the simulation cell of Au/C11TH.

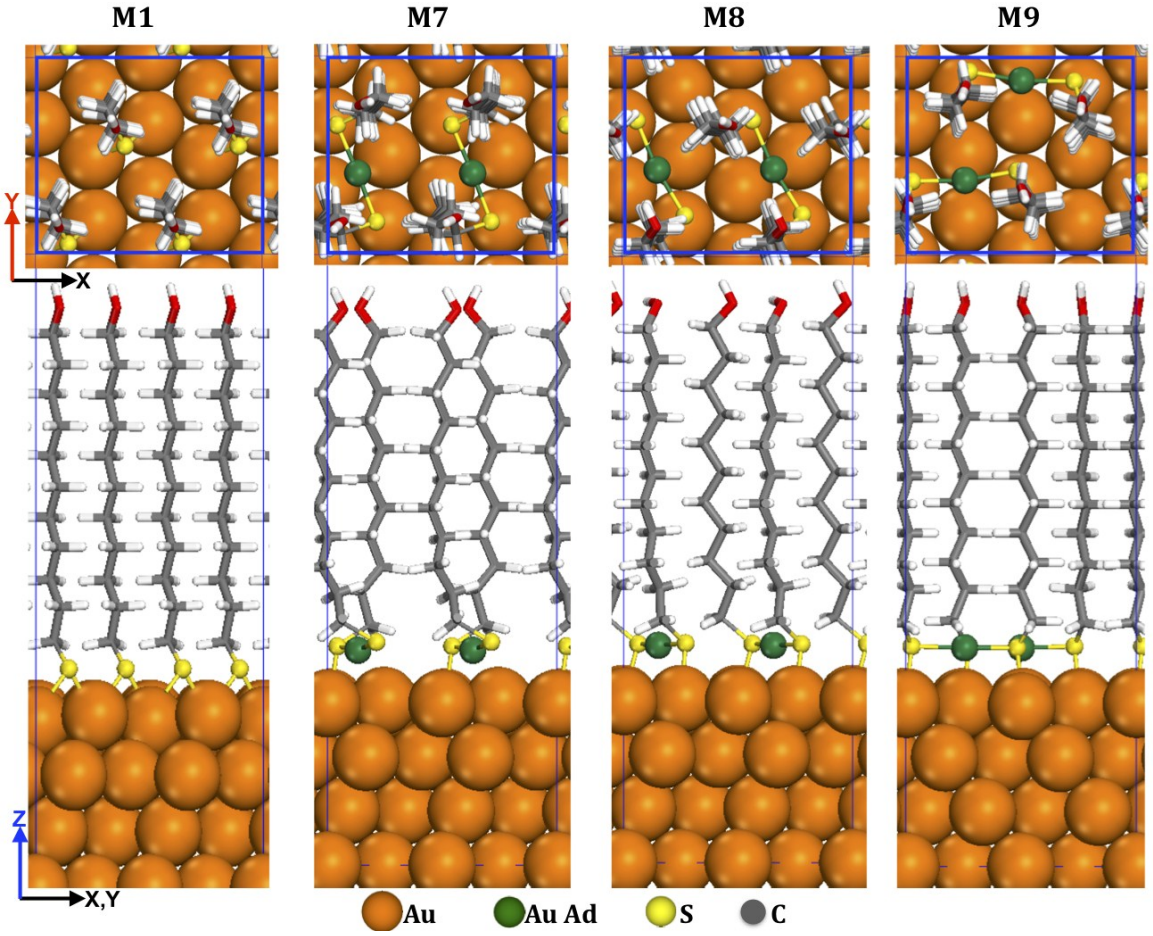

Figure S3: Tilt angle variation of the C11TH with different vectors with the use of optB86b functional in AIMD simulation. Schematic diagram to calculate tilt angle using different vectors.

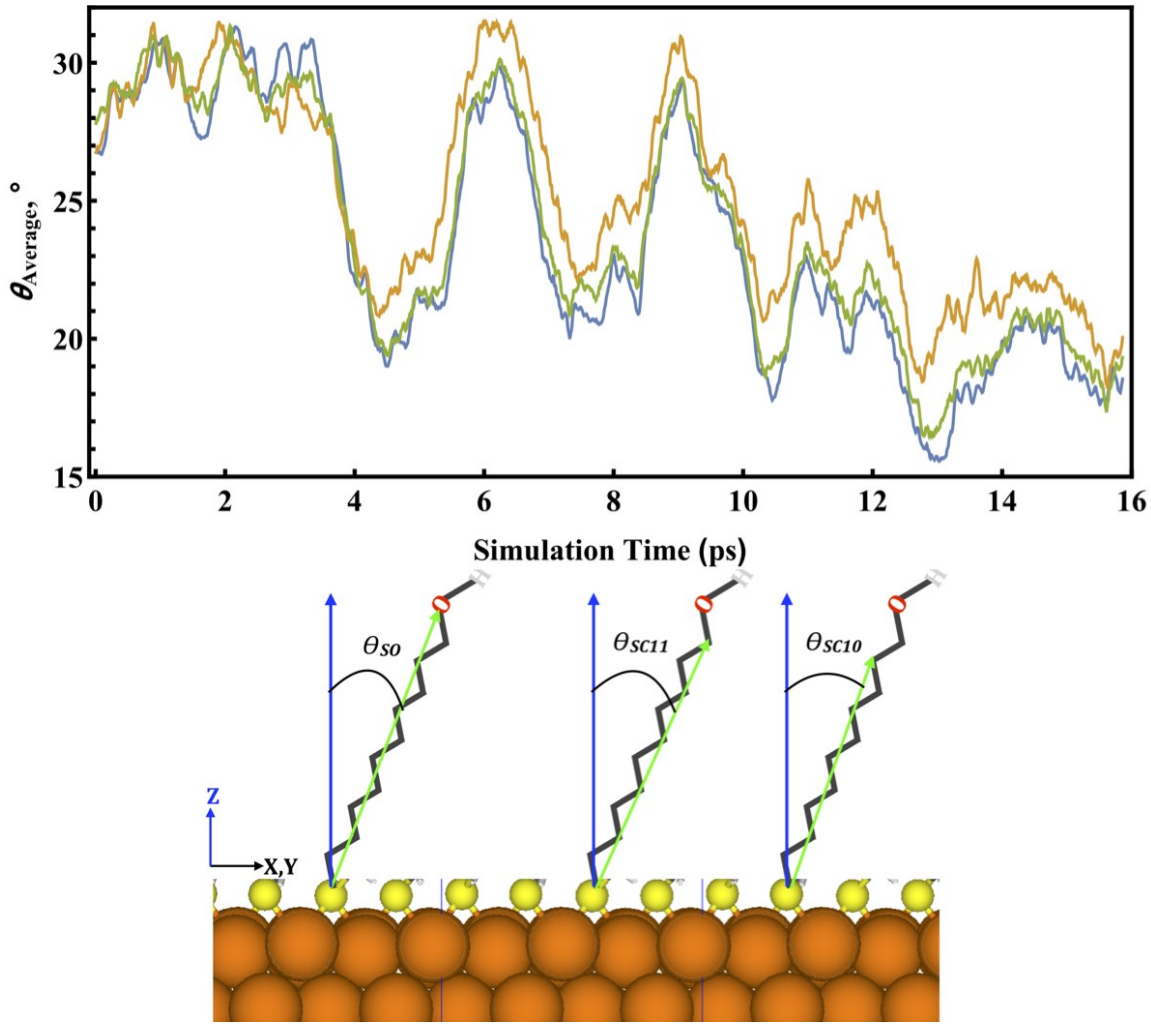

Figure S4: Snapshots obtained from AIMD simulation of M8/C11TH interface with the use of vdW density functional. Side view of different configurations with respect to *yz* plane Purple lines indicate the simulation cell of Au/C11TH. Color code: Orange (Au), Green (Au adatom), Yellow (Sulphur), Gray (Carbon), Red (Oxygen), White (Hydrogen). For the clarity hydrogens are not included except -OH.

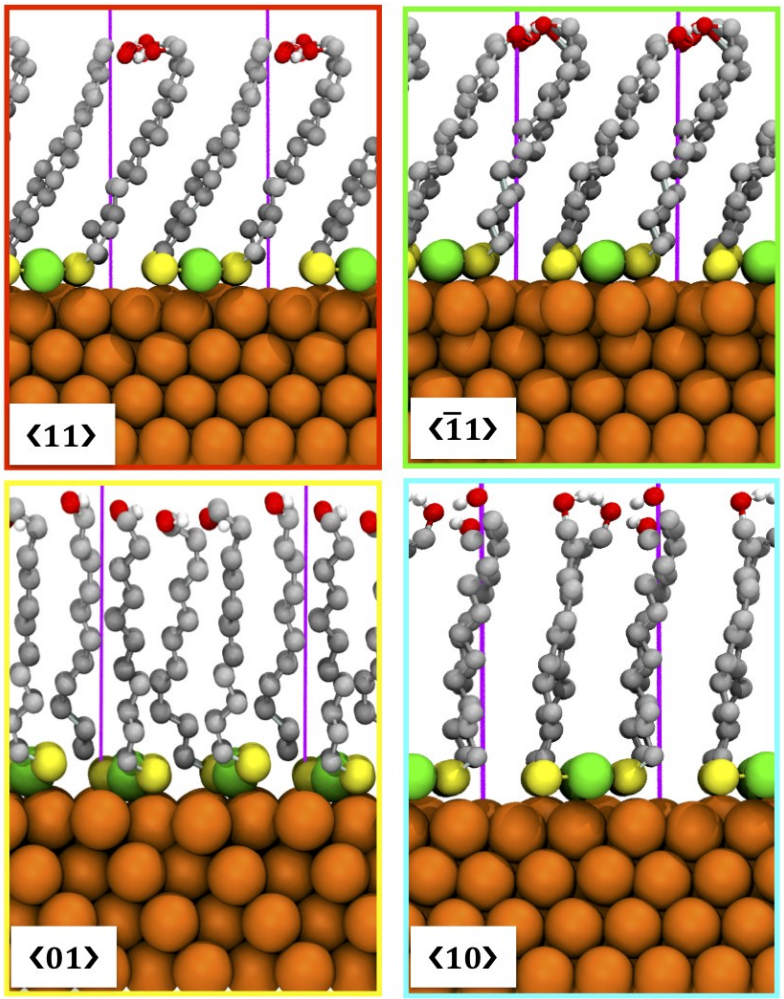

Table S1: Structural attributes of the studied Au(111)/C11TH with two different functionals in VASP. $\bar{\Delta}z$ and $\bar{\Delta}\theta$ indicates the thickness of C11TH in $\mathrm{\AA}$ and tilt angle formed by C11TH in $^{\circ}$, respectively.

Model	**With/Without Annealing**	$\bar{\Delta}z$ (Å)		$\bar{\Delta}\theta$ (°)	
		PBE	**optB86b**	**PBE**	**optB86b**
M1	No Annealing	15.17	15.08	6.80	7.10
	Annealing	13.91	13.48	25.3	46.5
	Difference	1.26	1.60	18.5	39.4
M7	No Annealing	14.90	14.73	9.30	9.30
	Annealing	14.73	13.29	15.3	21.4
	Difference	0.17	1.44	6.0	12.9
M8	No Annealing	15.03	14.99	7.90	7.90
	Annealing	14.30	12.64	20.5	23.9
	Difference	0.73	2.35	12.6	16
M9	No Annealing	15.14	15.00	6.90	6.9
	Annealing	14.78		13.5	
	Difference	0.36		6.6	