Evaluating the Terminal Group Switching of Responsive Monolayer Films: Examining Structural Rearrangements Via Molecular Simulations and Experimental Wetting Measurements: Supplementary Information

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Section S1: Switchable Surfaces mBuild Recipe

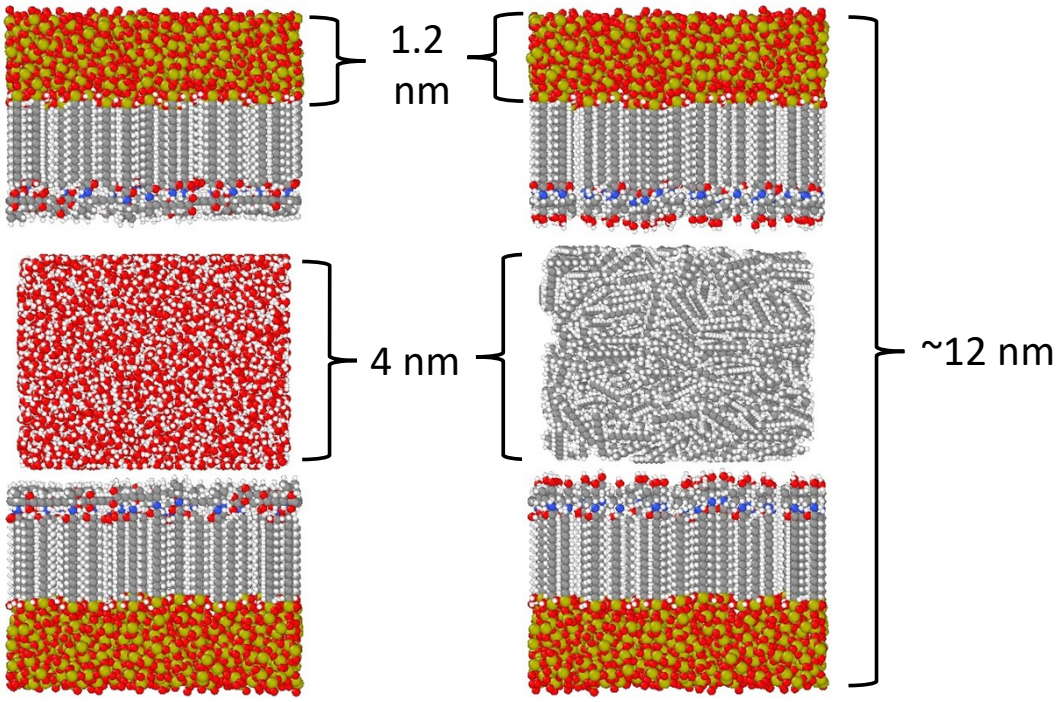


Figure S1: An image of the surfaces in the initial state under water (left) and *n*-hexane (right). Initially, the surfaces are solvated with enough distance between the two films to shield interactions between the terminal groups, and then the surfaces are compressed to form an STP bulk-liquid state, approximated by the center of mass of the slab, the bulk density, and the width of the liquid-surface interfacial region.

Table S1: Force field parameters.

Element	atom_type	epsilon (kJ/mol)	sigma (nm)	charge (elementary)	mass (amu)
C	opls_135	0.276144	0.35	-0.18	12.011
H	opls_140	0.12552	0.25	0.06	1.008
C	opls_136	0.276144	0.35	-0.12	12.011
O	opls_1001	0.71128	0.3	-0.43	15.999
Si	opls_1002	0.4184	0.4	0.86	28.085
O	opls_1008	0.71128	0.3	-0.215	15.999
O	opls_1007	0.71128	0.3	-0.215	15.999
C	opls_1004	0.276144	0.35	-0.12	12.011
C	opls_244B	0.276144	0.35	0.1	12.011
N	opls_238	0.71128	0.325	-0.48	14.007
H	opls_241	0	1	0.32	1.008
C	opls_235	0.43932	0.375	0.5	12.011
O	opls_236	0.87864	0.296	-0.5	15.999
C	opls_157	0.276144	0.35	0.145	12.011
O	opls_154	0.71128	0.312	-0.683	15.999
H	opls_155	0	1	0.418	1.008
Si	opls_1003	0.4184	0.4	0.745	28.085
O	opls_1005	0.71128	0.312	-0.683	15.999
H	opls_1006	0	1	0.418	1.008
H	opls_1009	0	0	0.215	1.008
O	tip3p_O	0.635968	0.31507524	-0.834	15.999
H	tip3p_H	0	1	0.417	1.008
C	opls_244	0.276144	0.35	0.1	12.011
C	opls_224B	0.276144	0.35	0.1	12.011
C	opls_267	0.43932	0.375	0.52	12.011
O	opls_269	0.87864	0.296	-0.44	15.999
O	opls_268	0.71128	0.3	-0.53	15.999
H	opls_270	0	1	0.45	1.008

Atom 1	Atom 2	k (kJ/mol /nm**2)	r_eq (nm)
CT	HC	284512	0.109
CT	CT	224262.4	0.1529
SI	OG	251040	0.165
SI	OH	251040	0.165
HO	OH	462750.4	0.0945
SI	CT	167360	0.185
C	CT	265265.6	0.1522
CT	N	282001.6	0.1449
H	N	363171.2	0.101
C	N	410032	0.1335
C	O	476976	0.1229
CT	OH	267776	0.141
tip3p_O	tip3p_H	462750.4	0.09572
C	O_3	476976	0.1229
C	OH	376560	0.1364

Atom 1	Atom 2	Atom 3	k (kJ/mol/rad**2)	theta_eq (rad)
HC	CT	HC	276.144	1.88146493
CT	CT	HC	313.8	1.93207948
CT	CT	CT	488.273	1.96698607
SI	OG	SI	167.36	2.530727
OG	SI	OG	502.08	1.919862
OH	SI	OG	502.08	1.919862
SI	OH	HO	198.96	2.1448
OH	SI	OH	502.08	1.919862
C	CT	HC	292.88	1.91113553
C	CT	CT	527.184	1.9390608
SI	CT	CT	254.97296	2.0944
SI	CT	HC	313.8	1.932079
HC	CT	N	292.88	1.91113553
CT	CT	N	669.44	1.91462619
CT	N	H	317.984	2.06646983
C	N	CT	418.4	2.12755636
C	N	H	292.88	2.09090444
CT	C	N	585.76	2.03505391
CT	C	O	669.44	2.10137642
N	C	O	669.44	2.14500965
CT	CT	OH	418.4	1.91113553
HC	CT	OH	292.88	1.91113553
CT	OH	HO	460.24	1.89368224
OG	SI	CT	502.08	1.7453
OH	SI	CT	502.08	1.7453
tip3p_H	tip3p_O	tip3p_H	836.8	1.82421813
C	CT	N	527.184	1.92160751
CT	C	O_3	669.44	2.10137642
CT	C	OH	585.76	1.88495559
O_3	C	OH	669.44	2.11184839
C	OH	HO	292.88	1.97222205

Atom 1	Atom 2	Atom 3	Atom 4	c0 (kJ/mol)	c1 (kJ/mol)	c2 (kJ/mol)	c3 (kJ/mol)	c4 (kJ/mol)	c5 (kJ/mol)
HC	CT	CT	HC	0.6276	1.8828	0	-2.5104	0	0
CT	CT	CT	HC	0.6276	1.8828	0	-2.5104	0	0
CT	CT	CT	CT	2.9288	-1.4644	0.2092	-1.6736	0	0
SI	*	*	*	0	0	0	0	0	0
*	SI	*	*	0	0	0	0	0	0
HC	CT	C	N	0	0	0	0	0	0
HC	CT	C	O	0	0	0	0	0	0
CT	CT	C	N	4.83252	-7.65254	1.68196	1.13805	0	0
CT	CT	C	O	4.87855	0	-4.87855	0	0	0
C	CT	CT	HC	-0.2092	-0.6276	0	0.8368	0	0
C	CT	CT	CT	-4.96013	6.28646	1.30959	-2.63592	0	0
H	N	CT	HC	0	0	0	0	0	0
C	N	CT	HC	-0.29079	-0.87237	0	1.16315	0	0
HC	CT	CT	N	0.97069	2.91206	0	-3.88275	0	0
CT	CT	CT	N	5.48732	0.02719	0	-5.51451	0	0
HC	CT	CT	OH	0.97905	2.93716	0	-3.91622	0	0
N	CT	CT	OH	14.4348	-11.00392	-3.43088	0	0	0
CT	CT	CT	OH	2.87441	0.58158	2.092	-5.54799	0	0
CT	CT	N	H	0	0	0	0	0	0
C	N	CT	CT	-4.707	2.92044	1.78656	0	0	0
CT	N	C	O	25.47638	0	-25.47638	0	0	0
H	N	C	O	20.5016	0	-20.5016	0	0	0
CT	C	N	CT	30.28798	-4.8116	-25.47638	0	0	0
CT	C	N	H	20.5016	0	-20.5016	0	0	0
CT	CT	OH	HO	-0.4435	3.83255	0.72801	-4.11705	0	0
HC	CT	OH	HO	0.9414	2.8242	0	-3.7656	0	0
HC	CT	C	O_3	0	0	0	0	0	0
HC	CT	C	OH	0	0	0	0	0	0
N	CT	C	O_3	0	0	0	0	0	0
N	CT	C	OH	14.4348	-11.00392	-3.43088	0	0	0
CT	CT	C	O_3	2.28446	0	-2.28446	0	0	0
CT	CT	C	OH	5.31786	0.7322	-2.28446	-3.7656	0	0
H	N	CT	*	0	0	0	0	0	0
C	CT	N	C	-10.35749	-29.58716	-1.16734	41.11199	0	0
CT	C	OH	HO	26.15	-3.138	-23.012	0	0	0
HO	OH	C	O_3	23.012	0	-23.012	0	0	0

Central Atom	Atom 1	Atom 2	Atom 3	k (kJ/mol)	phi_eq (rad)	n (dimensionless)
N	*	*	*	4.184	3.14159265	2
C	O	*	*	43.932	3.14159265	2
C	O_3	*	*	43.932	3.14159265	2

For more details on force fields used, please see the directory https://github.com/PTC-CMC/Switchable_Projects/blob/main/COOH_OH_systems/utils/Forcefields/oplsaa_charged.xml for the Foyer compatible force field file used.

Section S2: Simulation Methodology

$$Compression\ Steps = \frac{H}{R_{compress}}\left(\frac{\rho_{current}}{\rho_{target}} - 1\right) \quad \textbf{(Equation S1)}$$

Where –

H = current pore width in nm
$R_{compress}$ = Rate of compression = 0.001 nm/ps
$\rho_{current}$ = Current solvent density between top and bottom surfaces
ρ_{target} = Target solvent density between top and bottom surfaces

Calculated in Analysis/equilibration.py

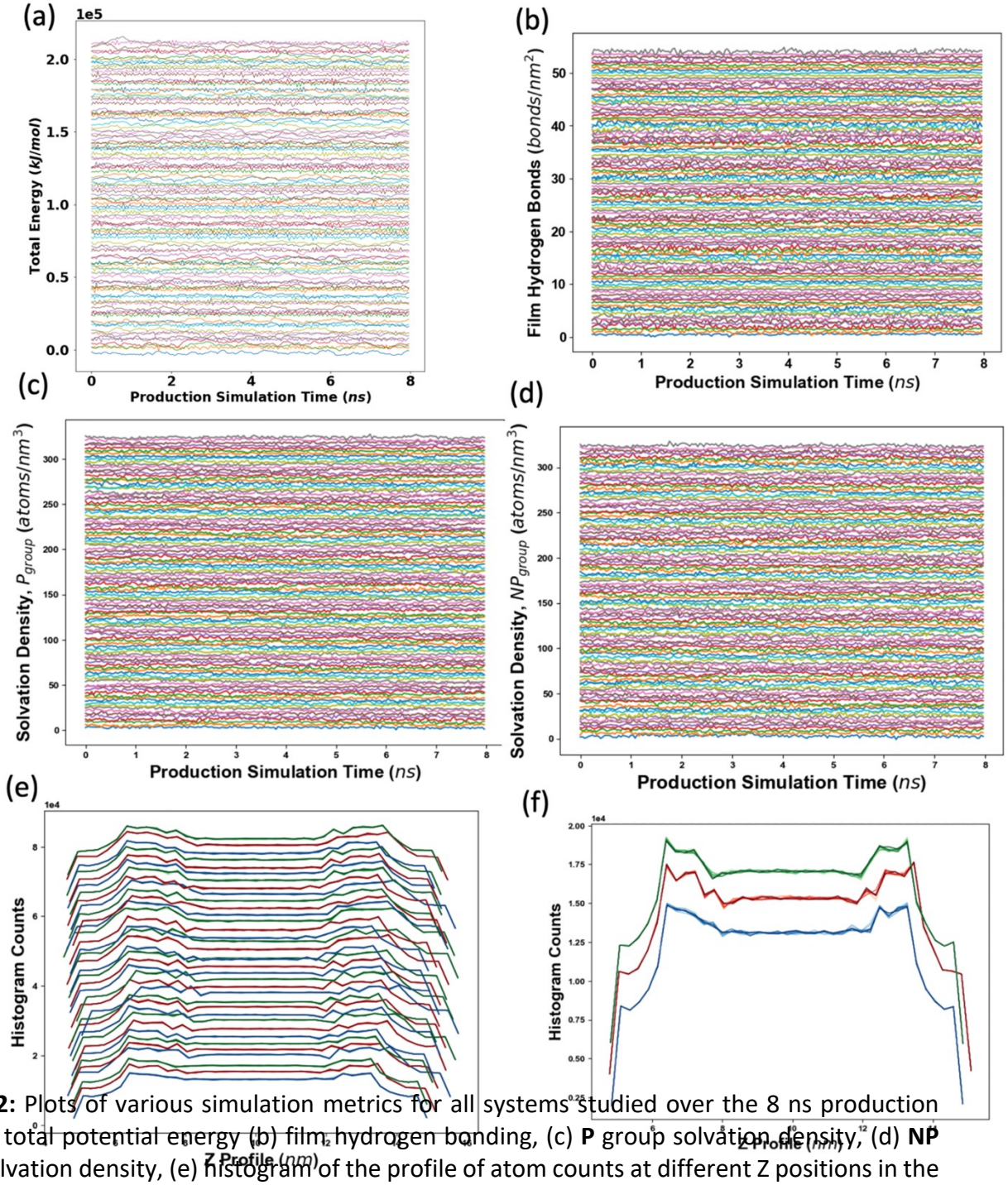


Figure S2: Plots of various simulation metrics for all systems studied over the 8 ns production runs. (a) total potential energy (b) film hydrogen bonding, (c) **P** group solvation density, (d) **NP** group solvation density, (e) histogram of the profile of atom counts at different Z positions in the simulation box, where every 0.4 ns, a new curve that is the average of that time interval is plotted, and (f) a zoomed in example of 3 curves from (e) that demonstrate the small oscillations that occur in the density profile over the course of the three simulations. All of the properties remain extremely stable over the 8 ns period indicating sufficient sampling time.

Section S3: Simulation Data

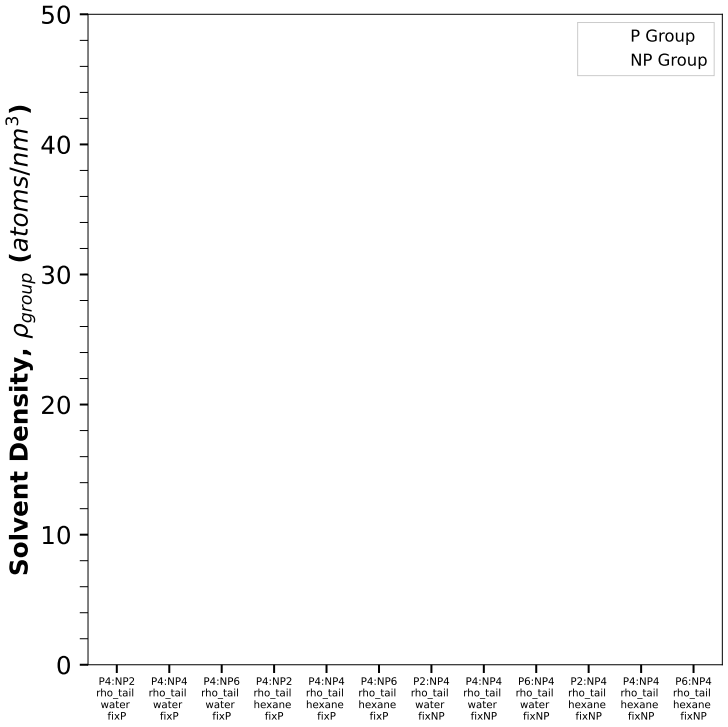


Figure S3: Solvent density affected by changing size of either **P** or **NP** group. First and third pairs of lines are in water, which show the blue **P** group line above the green **NP** group line. The second and fourth sets of points are done in hexane, which should show the reversed behavior for responsive switching surfaces. Related to Figure 4 of the Main Text.

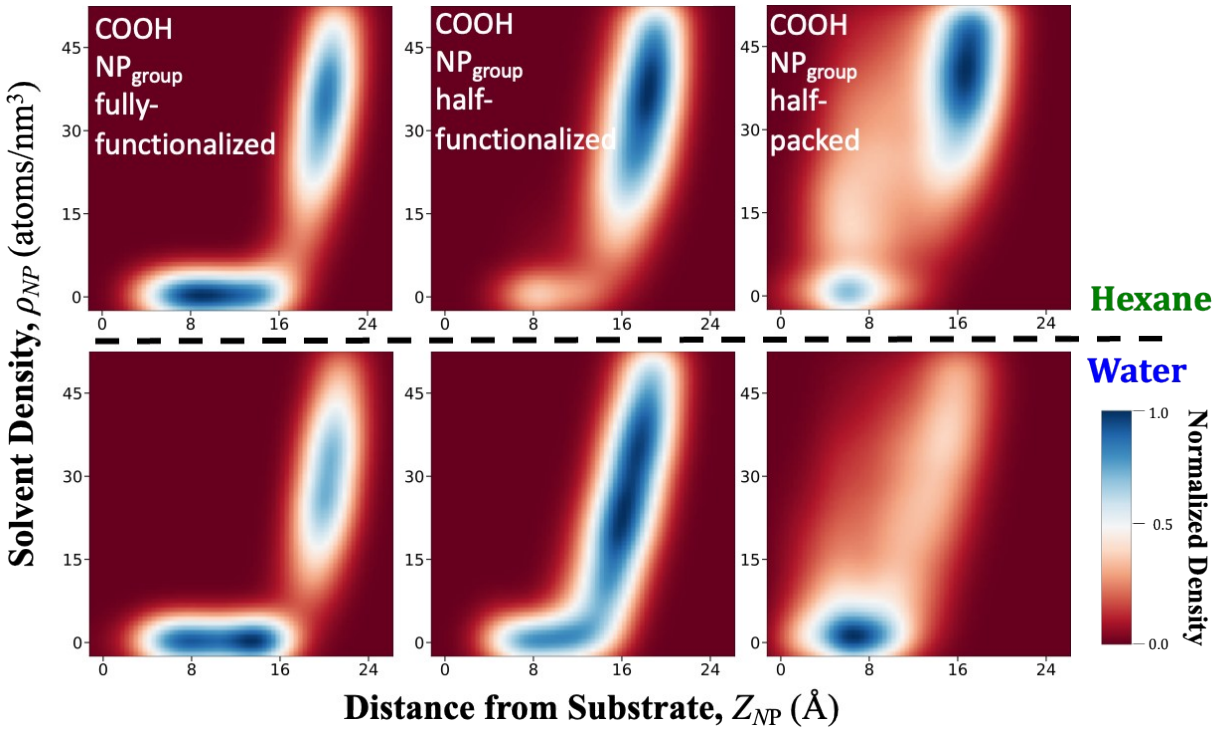


Figure S4: Heatmaps showing the distance from the substrate (Z_{NP}) versus solvent density (ρ_{NP}) for the carboxy P4:NP4 system in hexane (top) and water (bottom). Three variations of the carboxy P4:NP4 surfaces are shown: 4 chains per nm^2 density with no backfill chains and only functionalized chains (fully-functionalized, left), 4 chains per nm^2 density with half backfill chains and half functionalized chains (half-functionalized, middle), and 2 chains per nm^2 density with no backfill chains and only functionalized chains (half-packed, right). The backfill chains are 10-carbon alkylsilane chains in length and randomly placed between the functionalized chains.

Experimental and simulation correlation data for Figure 8: Multiple quantitative correlations are given for this this relationship: the root-mean square deviation is 21.8%, the slope is 221.2% with a p-value of 0.007, the Pearson correlation is 0.93 with a p-value of 0.0007, the Spearman correlation is 0.81 with a p-value of 0.015, and the Kendall Tau correlation is 0.67 with a p-value of 0.02. We note minor changes in the metrics that vary based on the extremes range provided by the control films, but all metrics give $p<0.05$.

Table S2: Data averaged from six different replicate surfaces and 100 chains per surface for ρ_{group}.

Solvent	Terminal Group	Chemistry	ρ_{NP}	95% CI	ρ_{P}	95% CI
water	P2:NP2	COOH	30.6	0.7	31.9	1.0
hexane	P2:NP2	COOH	34.2	1.4	20.9	1.8
water	P2:NP4	COOH	27.8	0.3	28.2	1.3
hexane	P2:NP4	COOH	37.8	0.6	17.2	1.0
hexane	P2:NP6	COOH	38.2	0.7	14.4	0.9
water	P2:NP6	COOH	27.5	1.1	23.6	0.9
water	P4:NP2	COOH	21.6	0.7	34.4	0.9
hexane	P4:NP2	COOH	26.1	0.7	20.2	0.9
water	P4:NP4	COOH	24.9	1.8	29.5	1.5
hexane	P4:NP4	COOH	31.6	1.3	16.2	1.3
water	P4:NP6	COOH	25.9	1.1	24.6	1.3
hexane	P4:NP6	COOH	30.3	2.2	15.0	1.5
water	P6:NP2	COOH	17.9	2.0	35.7	1.0
hexane	P6:NP2	COOH	18.3	1.8	23.1	3.0
hexane	P6:NP4	COOH	26.0	4.0	14.8	4.9
water	P6:NP4	COOH	22.8	3.0	30.6	3.9
hexane	P6:NP6	COOH	26.8	5.2	15.2	4.5
water	P6:NP6	COOH	22.9	4.2	27.3	4.6
hexane	P2:NP2	OH	30.8	0.6	20.1	0.6
water	P2:NP2	OH	26.7	1.4	44.2	1.2
water	P2:NP4	OH	22.2	1.0	37.7	0.7
hexane	P2:NP4	OH	33.2	0.7	15.0	0.7
water	P2:NP6	OH	22.6	1.2	33.6	1.4
hexane	P2:NP6	OH	34.9	0.6	13.4	1.0
water	P4:NP2	OH	21.7	1.2	45.2	1.2
hexane	P4:NP2	OH	25.6	0.6	20.0	0.8
hexane	P4:NP4	OH	31.7	2.4	14.4	1.8
water	P4:NP4	OH	21.7	1.6	39.5	2.1
water	P4:NP6	OH	22.6	1.7	35.4	2.6
hexane	P4:NP6	OH	34.4	1.0	10.5	0.8
water	P6:NP2	OH	16.1	1.1	45.9	1.4
hexane	P6:NP2	OH	20.0	1.3	20.1	1.6
hexane	P6:NP4	OH	23.5	2.4	16.6	1.9
water	P6:NP4	OH	15.0	1.1	44.7	1.5
hexane	P6:NP6	OH	26.6	2.9	14.2	2.4
water	P6:NP6	OH	24.5	3.0	31.6	4.7

Table S3: Data averaged from six different replicates and 100 chains per surface for Z_{group}.

Solvent	Terminal Group	Chemistry	Z_{NP}	95% CI	Z_P	95% CI
water	P2:NP2	COOH	14.3	0.1	14.6	0.1
hexane	P2:NP2	COOH	16.0	0.2	15.1	0.3
water	P2:NP4	COOH	15.0	0.1	15.0	0.1
hexane	P2:NP4	COOH	17.5	0.1	14.9	0.2
hexane	P2:NP6	COOH	19.2	0.3	14.7	0.1
water	P2:NP6	COOH	15.9	0.3	15.0	0.1
water	P4:NP2	COOH	14.1	0.1	15.7	0.2
hexane	P4:NP2	COOH	15.2	0.2	14.9	0.2
water	P4:NP4	COOH	15.1	0.3	15.8	0.2
hexane	P4:NP4	COOH	16.7	0.4	14.7	0.3
water	P4:NP6	COOH	16.1	0.4	15.9	0.2
hexane	P4:NP6	COOH	17.0	0.6	15.1	0.3
water	P6:NP2	COOH	14.2	0.3	16.9	0.3
hexane	P6:NP2	COOH	14.9	0.2	16.7	0.8
hexane	P6:NP4	COOH	16.6	0.9	15.5	1.3
water	P6:NP4	COOH	15.8	0.8	16.9	0.6
hexane	P6:NP6	COOH	17.3	1.5	16.2	1.0
water	P6:NP6	COOH	16.5	1.2	17.1	1.0
hexane	P2:NP2	OH	15.4	0.2	14.8	0.2
water	P2:NP2	OH	13.8	0.1	15.3	0.2
water	P2:NP4	OH	14.1	0.2	15.5	0.1
hexane	P2:NP4	OH	16.4	0.2	14.6	0.2
water	P2:NP6	OH	14.7	0.3	15.7	0.2
hexane	P2:NP6	OH	17.9	0.4	14.6	0.2
water	P4:NP2	OH	14.0	0.3	16.4	0.3
hexane	P4:NP2	OH	14.9	0.3	15.4	0.2
hexane	P4:NP4	OH	16.9	0.5	14.8	0.4
water	P4:NP4	OH	14.8	0.4	16.5	0.4
water	P4:NP6	OH	15.2	0.5	16.8	0.4
hexane	P4:NP6	OH	18.9	0.3	14.5	0.3
water	P6:NP2	OH	13.8	0.2	17.8	0.4
hexane	P6:NP2	OH	14.9	0.2	16.4	0.5
hexane	P6:NP4	OH	16.0	0.6	16.0	0.7
water	P6:NP4	OH	14.4	0.4	18.4	0.3
hexane	P6:NP6	OH	17.3	1.1	16.2	0.7
water	P6:NP6	OH	17.2	1.1	17.0	0.8

Table S4: Data averaged from six different replicates and 100 chains per surface for θ_{group}.

Solvent	Terminal Group	Chemistry	ϑ_{NP}	95% CI	ϑ_{P}	95% CI
water	P2:NP2	COOH	7	2	16	3
hexane	P2:NP2	COOH	35	2	11	4
water	P2:NP4	COOH	9	2	18	2
hexane	P2:NP4	COOH	41	1	9	2
hexane	P2:NP6	COOH	45	2	7	1
water	P2:NP6	COOH	14	3	17	2
water	P4:NP2	COOH	0	3	29	2
hexane	P4:NP2	COOH	21	1	9	3
water	P4:NP4	COOH	10	5	27	4
hexane	P4:NP4	COOH	31	5	5	4
water	P4:NP6	COOH	14	4	24	3
hexane	P4:NP6	COOH	22	6	10	4
water	P6:NP2	COOH	3	4	31	3
hexane	P6:NP2	COOH	10	7	24	8
hexane	P6:NP4	COOH	28	13	11	13
water	P6:NP4	COOH	18	10	27	7
hexane	P6:NP6	COOH	24	14	18	12
water	P6:NP6	COOH	18	12	29	11
hexane	P2:NP2	OH	22	3	8	1
water	P2:NP2	OH	-5	4	37	4
water	P2:NP4	OH	-2	3	35	2
hexane	P2:NP4	OH	27	3	6	3
water	P2:NP6	OH	1	4	33	2
hexane	P2:NP6	OH	31	4	3	3
water	P4:NP2	OH	-2	4	35	2
hexane	P4:NP2	OH	15	3	15	2
hexane	P4:NP4	OH	31	8	4	6
water	P4:NP4	OH	6	6	33	4
water	P4:NP6	OH	5	6	33	5
hexane	P4:NP6	OH	40	3	-3	4
water	P6:NP2	OH	-3	3	37	3
hexane	P6:NP2	OH	13	4	18	5
hexane	P6:NP4	OH	21	9	15	6
water	P6:NP4	OH	0	5	39	4
hexane	P6:NP6	OH	25	10	16	7
water	P6:NP6	OH	26	11	24	9

Table S5: Data across 6 surfaces and 100 chains per surface for solvent accessible surface area (SASA), film thickness, and film number of hydrogen bonds.

Solvent	Terminal Group	Chemistry	SASA	95% CI	Film Thickness	95% CI	Film H-bonds	95% CI
water	P2:NP2	COOH	1.64	0.09	19.8	0.2	0.10	0.02
hexane	P2:NP2	COOH	1.66	0.14	19.9	0.1	0.58	0.03
water	P2:NP4	COOH	1.87	0.07	21.4	0.1	0.14	0.01
hexane	P2:NP4	COOH	1.98	0.12	22.1	0.2	0.50	0.03
hexane	P2:NP6	COOH	2.40	0.12	24.3	0.1	0.53	0.03
water	P2:NP6	COOH	1.93	0.07	23.1	0.2	0.16	0.02
water	P4:NP2	COOH	1.82	0.06	20.7	0.1	0.11	0.01
hexane	P4:NP2	COOH	1.75	0.07	20.1	0.3	0.54	0.01
water	P4:NP4	COOH	1.90	0.05	21.5	0.1	0.15	0.02
hexane	P4:NP4	COOH	1.95	0.06	21.8	0.2	0.50	0.02
water	P4:NP6	COOH	1.97	0.05	23.3	0.1	0.16	0.02
hexane	P4:NP6	COOH	2.18	0.10	24.1	0.3	0.51	0.02
water	P6:NP2	COOH	1.90	0.09	22.4	0.2	0.08	0.01
hexane	P6:NP2	COOH	1.84	0.09	21.8	0.4	0.64	0.03
hexane	P6:NP4	COOH	1.94	0.05	22.4	0.2	0.56	0.08
water	P6:NP4	COOH	1.99	0.02	22.7	0.3	0.11	0.04
hexane	P6:NP6	COOH	2.03	0.07	24.0	0.2	0.60	0.04
water	P6:NP6	COOH	1.95	0.02	23.5	0.2	0.12	0.04
hexane	P2:NP2	OH	1.56	0.12	19.6	0.3	1.02	0.04
water	P2:NP2	OH	1.67	0.10	19.4	0.2	0.23	0.03
water	P2:NP4	OH	1.81	0.06	20.9	0.2	0.32	0.02
hexane	P2:NP4	OH	1.88	0.07	21.8	0.2	1.03	0.05
water	P2:NP6	OH	1.93	0.04	22.4	0.1	0.38	0.04
hexane	P2:NP6	OH	2.35	0.07	23.8	0.1	1.01	0.03
water	P4:NP2	OH	1.90	0.06	21.2	0.1	0.21	0.02
hexane	P4:NP2	OH	1.80	0.10	20.4	0.2	1.03	0.08
hexane	P4:NP4	OH	2.03	0.07	22.0	0.1	1.07	0.03
water	P4:NP4	OH	1.97	0.08	21.4	0.1	0.27	0.02
water	P4:NP6	OH	1.95	0.04	23.0	0.2	0.33	0.05
hexane	P4:NP6	OH	2.26	0.07	24.2	0.3	1.03	0.03
water	P6:NP2	OH	1.99	0.07	22.8	0.2	0.20	0.03
hexane	P6:NP2	OH	1.93	0.04	22.8	0.2	1.01	0.03
hexane	P6:NP4	OH	2.00	0.06	22.6	0.3	1.02	0.05
water	P6:NP4	OH	2.01	0.05	22.9	0.3	0.20	0.02
hexane	P6:NP6	OH	2.13	0.06	23.9	0.3	1.03	0.05
water	P6:NP6	OH	2.03	0.04	23.6	0.1	0.37	0.07

Table S6: Measured parameters for fully-functionalized (i.e. 0% backfill chains on surface) and half-packed (i.e. 2 ch/nm^2 packing density) P4:NP4 carboxyl films.

Solvent	Terminal Group	Chemistry	Surface Type	ρ_{NP}	95% CI	ρ_P	95% CI
water	P4:NP4	COOH	fully-functionalized	20.5	0.8	16.6	0.8
hexane	P4:NP4	COOH	fully-functionalized	16.9	0.4	11.8	0.4
water	P4:NP4	COOH	half-packed	23.5	1.7	32.2	1.7
hexane	P4:NP4	COOH	half-packed	33.5	1.6	19.6	0.9

Solvent	Terminal Group	Chemistry	Surface Type	Z_{NP}	95% CI	Z_P	95% CI
water	P4:NP4	COOH	fully-functionalized	15.9	0.1	17	0.1
hexane	P4:NP4	COOH	fully-functionalized	15.7	0.2	16.9	0.1
water	P4:NP4	COOH	half-packed	10.2	0.3	11.6	0.6
hexane	P4:NP4	COOH	half-packed	12.7	0.4	12.3	0.7

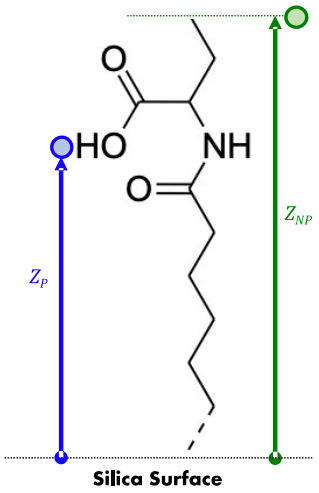
Solvent	Terminal Group	Chemistry	Surface Type	ϑ_{NP}	95% CI	ϑ_P	95% CI
water	P4:NP4	COOH	fully-functionalized	19	2	42	2
hexane	P4:NP4	COOH	fully-functionalized	16	2	39	2
water	P4:NP4	COOH	half-packed	-5	6	20	5
hexane	P4:NP4	COOH	half-packed	10	4	6	4

Solvent	Terminal Group	Chemistry	Surface Type	SASA	95% CI	Film Thickness	95% CI	Film Hbond	95% CI
water	P4:NP4	COOH	fully-functional-ized	2.08	0.02	23.4	0.17	0.14	0.11
hexane	P4:NP4	COOH	fully-functional-ized	2.06	0.05	23.3	0.2	0.28	0.22
water	P4:NP4	COOH	half-packed	2.18	0.15	19.8	0.6	0.06	0.05
hexane	P4:NP4	COOH	half-packed	2.45	0.16	20.9	0.5	0.24	0.20

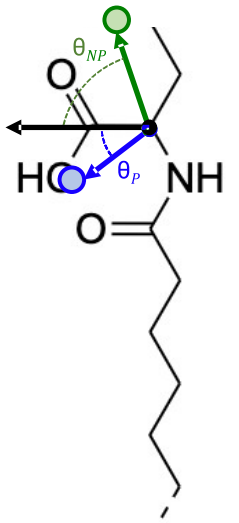
Section S4: Glossary of parameters

1. Mathematical Equations/Definitions for Variables

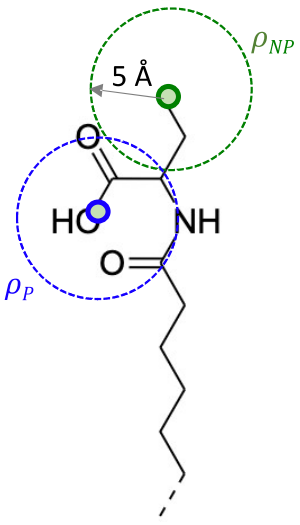
   a. <u>Per chain quantities</u>



Metric: Tail positions
Symbol: Z_{group}
This is the average distance for the atom terminal group tail, non-polar (**NP**) or polar (**P**), from the solid silica surface. The silica surface is set at the average position for the top level of silicon atoms, which are part of the amorphous lattice. For the polar tail, this is considered the oxygen atom of the hydroxyl group and the oxygen atom bonded to a hydrogen in the carboxyl group. This measure captures the distance these atoms are along the surface normal, where the positive direction indicates an atom closer to the solvent region.



Metric: Tail orientation
Symbol: θ_{group}
This is the average angle the vector comprising of the terminal atom of the **NP** or **P** tail and the base of the terminal group, known as the pivot carbon, make with the surface plane. It seeks to capture the orientational preference for one tail to stick outwards (value of 90°) and a tail sticking back toward into the coating (value <0°).



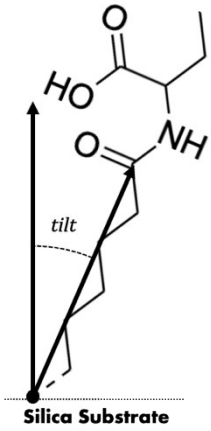
Metric: Tail solvation shell
Symbol: ρ_{group}
This value is the is the average total number of solvent atoms found within a 5 Ångstrom distance of the specified **P** or **NP** tail. The number was chosen as this has been related to the sensing depth of chemical moieties in self-assembled monolayer structures (Laibinis *et al.* 1995). This metric gives an approximation of the relative spacing of the tail to the given solvent, with a maximum value of ~53 atoms in the bulk water solvation shell and ~48 atoms in the bulk hexane shell, based on the raw density values of 1.01 g/cm^3 and 0.66 g/cm^3, respectively.

Equation for maximum atoms in solvation shell:
$max\ atoms = density * n_A * n_{atoms} * Volume/10^{30}/mwt$

Metric: Intrafilm hydrogen bonds
Symbol: Film H-bonds

The hydrogen bonds are found via the MDAnalysis Python package, under the Hydrogen Bond Analysis module. The acceptor atoms are determined as any atom of nitrogen or oxygen in the terminal group or chain backbone, and the donors are any of those atoms with a covalent hydrogen bond. A hydrogen bond is determined to have occurred if the donor to acceptor distance is less than a cutoff of 0.3 nm and the angle between the acceptor-hydrogen-donor is greater than 120° (chosen to slightly increase sampling rate). The number of these bonds that exist at each simulation time is summed for each chain, and then the total is averaged over the entire simulation trajectory. This gives an approximation of the capability for these chains to interact with neighboring chains. For example, a single carboxyl terminated terminal group could form 2 donation hydrogen bonds but has 4 acceptor atoms in the chain to have a maximum of ~6 hydrogen bonding locations.

Metric: Chain tilt
Symbol: α
The tilt angle of the chain is an indication of chain packing across the surface. This value is the vector angle measured from the silica atom of the silane chain headgroup to the alpha carbon in the amide group, compared to the surface normal vector. A value of 0° indicates a chain that is completely upright, as seen in the figure to the right. Tight packing of chains leads to values closer to 0° and looser packings to values greater than 0°.



b. <u>Block Averaging</u>

Averages and 95% Cis are generated by first averaging all 200 simulation frames, and for each chain on the surface. This is done for six different surfaces, three replicates with two unique coatings per surface. s_{group} is the sample standard deviation, $n_{surface}$ is the number of surfaces, 6, and $Z_{95\%}$ is a 95% Z-score for a two sided hypothesis test.

$$X_{group} = \frac{1}{n_{surface}} \sum_{1}^{n_{surface}} X_{group}, \quad 95\%\ CI\ X_{group} = \frac{s_{group}}{\sqrt{n_{surface}}} * Z_{95\%}$$

c. Total Surface Properties

The total surface properties are measures that are obtained over the whole surface. Any value with the Δ refers to a difference between the **NP** and **P** tails for the given value means, μ. This difference is taken respective to the solvent that the value is obtained for; if under hexane, the value is the μNP - μP, and if under water the value is μP - μNP. The intention is that positive values indicate the surface is in the preferred state.

$$\Delta X_{wat} = \bar{X}_P - \bar{X}_{NP}, \quad \Delta_{hex} = \bar{X}_{NP} - \bar{X}_P$$

Metric: Difference in tail positions
Symbol: ΔZ_{sol}
This value looks at the difference in Z in the tail positions calculated for the averaged tail quantity and looks for the preference of a given tail with respect to the environment of interest. For water, we would expect the P group to be more positive in a responsive switching surface, so we take the difference of the Z_p and Z_{NP} to get the state of the surface under that solvent.

Metric: Difference in tail orientation
Symbol: $\Delta\theta_{sol}$
The difference in angles is generated similarly to the difference in positions, where a more positive value should always indicated a more dynamic switching state.

Metric: Difference in tail solvent shell
Symbol: $\Delta\rho_{sol}$
The ρ_{sol} metric also has the benefit of something that should be low for ρ_{NP} in water and high for the P tail. A more positive value indicates a better state for either surface.

Metric: Solvent accessible surface area
Symbol: SASA
The solvent accessible surface area, known as SASA, is a key technique used to understand the contactable surface available for a soft particle or molecule. Instead of having a well-defined surface, molecules have an approximate interaction regime, defined by their Van d

Metric: Film thickness
Symbol: *h*
The surface thickness gives us some idea of how favorably the surface interacts with the solvent, i.e. does it compact itself to reduce surface exposure, or allow for some solvation to occur between favorable interactions. This is measured from the average position of the top layer of silicon surface atoms in the silica, to the outermost position of the terminal groups.

Section S5: Experimental Details

Figure S4 shows the preparation of functionalized monolayers from a vinyl-terminated film by sequential surface reactions on the vinyl groups. Monolayers having terminal vinyl groups showed a sessile water contact angle of 97 ± 1˚, which indicates the formation of a well-packed film. Mixed monolayers having vinyl- and methyl-terminated groups in a 1:1 composition presented a contact angle of 101 ± 1˚, showing the increase in hydrophobicity as methyl-terminated adsorbates are added. After exposing these vinyl-terminated precursors to a $KMnO_4/NaIO_4$ oxidizing solution, the observed water contact angle decreased to 58 ± 2˚ and 81 ± 2˚ for the packed and mixed composition, as expected from the formation of a more hydrophilic surface as the vinyl groups were converted into $-CO_2H$ moieties. The film was then reacted with $SOCl_2$ to form an acyl chloride-rich surface, which can react with various bifunctional amines. The resulting bifunctional monolayers feature a chemically heterogeneous surface composition consisting of hydrophilic and hydrophobic moieties. The characterization of the surface properties of these monolayers was evaluated through wettability measurements and the results are shown in Figure 6 of the main text. These measurements show the multi-functionality of these monolayers in contrast to the contact angles from $-CH_3$, -OH, and $-CO_2H$ control surfaces shown in Table S7.

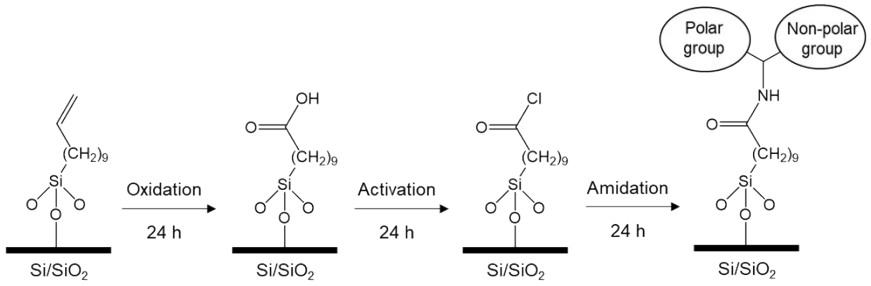


Figure S5. Scheme showing the approach to fabricate functionalized monolayers via sequential surface reactions on a vinyl-terminated precursor. Backfilling adsorbates are not shown in the scheme.

Table S7. Characterization of Control Monolayers with Water (θ_{H2O}) and α-Bromonaphthalene ($\theta_{\alpha BN}$) Sessile Contact Angle (degrees).

Monolayers	Sessile Contact Angles			
	θ_{H2O}	95% CI	$\theta_{\alpha BN}$	95% CI
Au / C_{11}-OH	31	2	18	1
Si / C_9-CO_2H	58	2	20	1
Si / C_7-CH_3 + C_9-CO_2H (1:1 composition)	81	2	39	1
Si / C_7-CH_3	105	1	50	2

The synthetic steps described above were validated by ATR-FTIR using porous silicon (PSi) as substrate in Figure S5. Flat Si/SiO_2 was replaced by PSi for the spectroscopic analysis since the latter has higher surface area that increases the amount of coating material. Figure S2 shows the

IR spectra of the functional groups composing the film in each reactive step. The vinyl-terminated monolayer shows characteristic absorption bands due to stretching of the C-H bonds in the methylene groups (ν_s 2927 cm^{-1}; ν_{as} 2857 cm^{-1}), and the absorption bands related to the vinyl functional group (-C=C stretch, 1640 cm^{-1}; =CH stretch, 3080 cm^{-1}). After the oxidation, a peak at 1714 cm^{-1} appears due to the C=O stretching vibration of the -CO_2H moieties and the vinyl-related peaks disappear. The functionalization step with amine-containing functional groups is shown here with the attachment of Leucine (-CO_2H as the polar group). This amide surface attachment of Leucine is associated with the appearance of an amide I peak at 1658 cm^{-1}. As observed, a peak corresponding to the -CO_2H groups is still observed at 1713 cm^{-1}, due to polar group in the functionalizing molecule. The similarity in the area of the peaks at 1713 and 1658 cm^{-1} reflects the expected composition of the Leucine terminated film, with an approximate 1:1 ratio between the carboxylic acid and the amide group in the structure.

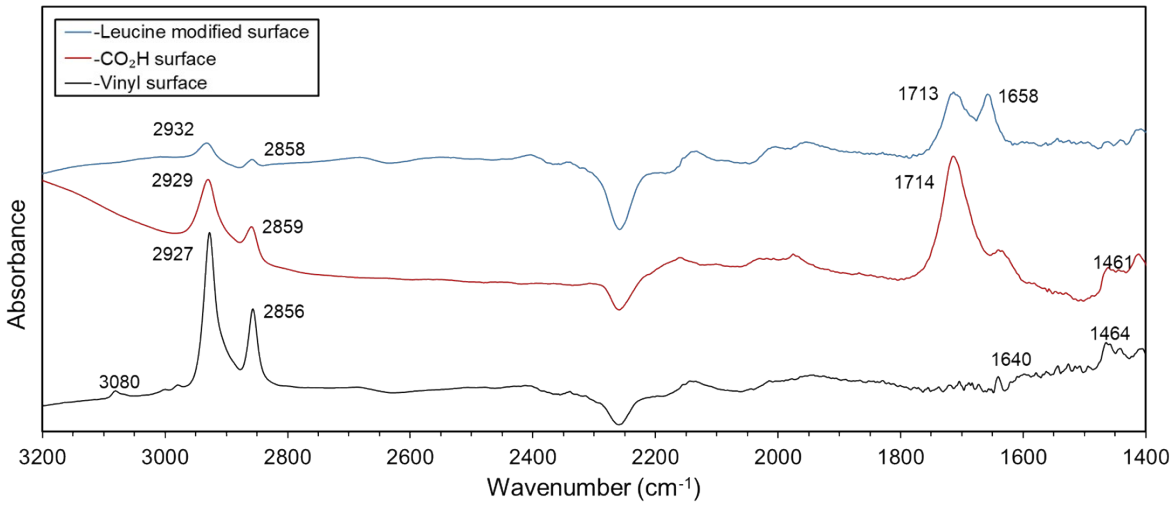


Figure S6. ATR-FTIR spectra of a (a) vinyl, (b) carboxylic acid, (c) Leucine-terminated film on PSi substrates.

Table S8. Hydroxyl terminated experimental contact angles. First row of values is the triplicate mean, and the second row is the standard deviation.

	Contact Angles for -OH Polar side (degrees)			
	Fully-functionalized		Half-functionalized	
Sample	**aBN**	**Water**	**aBN**	**Water**
P2-NP0	12	66	30	78
	1	2	1	1
P2-NP1	16	63	32	80
	1	1	1	2
P2-NP2	16	60	39	86
	2	1	1	2
P2-Isopropyl	19	58	41	86
	0	1	1	1
P2-NP3	17	59	35	82
	2	2	1	1
P2-NP4	19	60	37	80
	1	4	2	2

Table S9. Carboxyl terminated experimental contact angles. First row of values is the triplicate mean, and the second row is the standard deviation.

	Contact Angles for -COOH Polar side (degrees)			
	Fully-functionalized		Half-functionalized	
Sample	**aBN**	**Water**	**aBN**	**Water**
P2-NP0	18	59	33	78
	2	2	2	2
P2-NP1	17	58	33	79
	3	1	1	2
P2-NP2	14	59	36	84
	3	2	1	1
P2-Isopropyl	17	59	33	79
	1	2	2	1
P2-NP3	20	66	34	79
	1	2	2	3
P2-NP4	17	65	36	81
	2	2	2	1

Section S6: Installing and operating related code

1. Installation

The main data will be held in Switchable_Projects downloaded from https://github.com/PTC-CMC/Switchable_Projects.git

```
mkdir Switchable-Data
cd Switchable-Data
git clone https://github.com/CalCraven/switchable_interfaces
cd switchable_interfaces
conda env create -f environment.yml
conda activate switchable39
pip install .
cd ..
git clone https://github.com/CalCraven/surface_coatings
cd surface_coatings
git checkout switchable_al
pip install .
cd ..
git clone https://github.com/PTC-CMC/Switchable_Projects.git
cd Switchable_Projects
```

Note that the cloned GitHub repositories do not contain the raw trajectories, just the code for generating the trajectories and analysis. To obtain the trajectories, please download and unzip the Switchable_Projects directory from https://zenodo.org/records/15176320 instead of from https://github.com/PTC-CMC/Switchable_Projects.git.

2. Operating workflows

```
cd Switchable-Data/Switchable_Projects/COOH_OH_systems # skip if you're already
here
conda activate switchable39
python init_project.py
python project.py status
python project.py run -o build_surface
python project.py -o copy_run_files_rahman
python project.py submit -o run_simulations
python project.py run -o generate_data
python analysis_project.py run -o calculate_surface_averages
cd ../Packing_systems
conda activate switchable39
python init_project.py
python project.py status
python project.py run -o build_surface
python project.py -o copy_run_files_rahman
python project.py submit -o run_simulations
python project.py run -o generate_data
python analysis_project.py run -o calculate_surface_averages
```