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

Supporting Information for The Molecular Configuration of a DOPA/ST Monolayer at Air-Water Interface: A Molecular Dynamics Study

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Assigned force field types for DOPA and ST are list for reproduce the simulation:

I DOPA

Carbon in alkyl tails:OPLS_157 and OPLS_158

Hydrogen in alkyl tails: OPLS_140

O=C-N-H: OPLS_235, OPLS_236, OPLS_238, OPLS_241

CH2 in N-CH2: OPLS_244

C and H in aromatic ring: OPLS_145, OPLS_146

Hydroxyl: OPLS_167 and OPLS_155

II ST

Carbon in alkyl tails:OPLS_157 and OPLS_158

Hydrogen in alkyl tails: OPLS_140

C and H in aromatic ring: OPLS_145, OPLS_146

Hydroxyl: OPLS_167 and OPLS_155

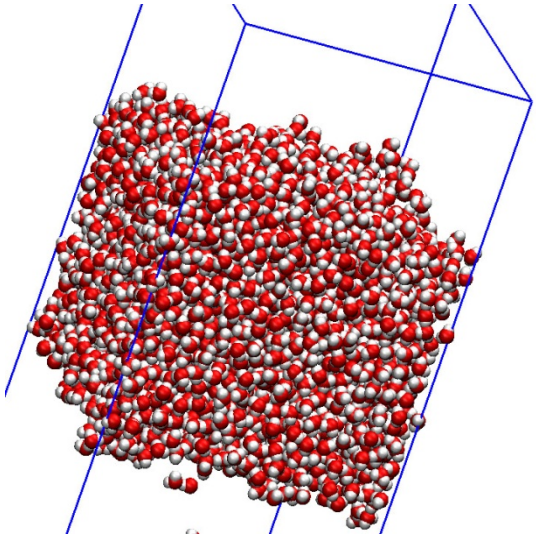


Figure S1 Cell box of water simulation.

A box of 5.0×5.0×20.0 nm^3 containing 4320 water molecules.

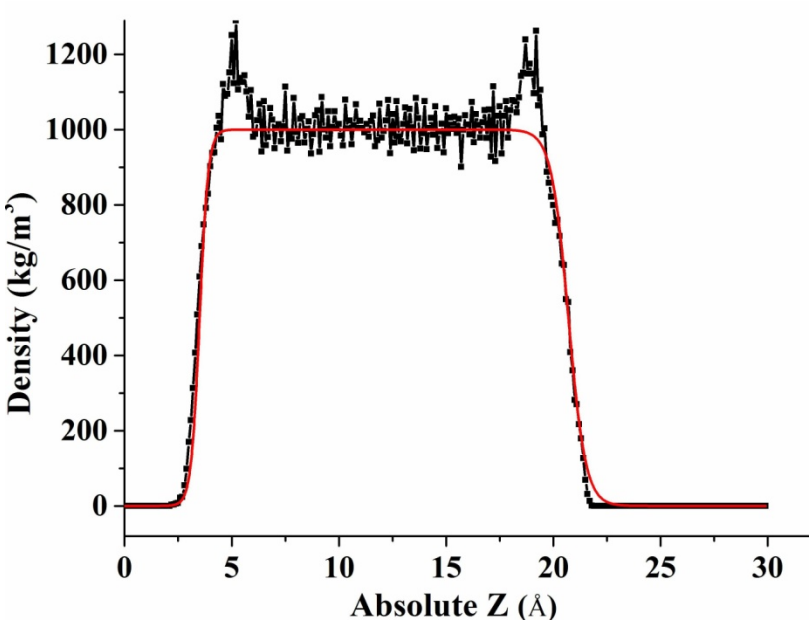
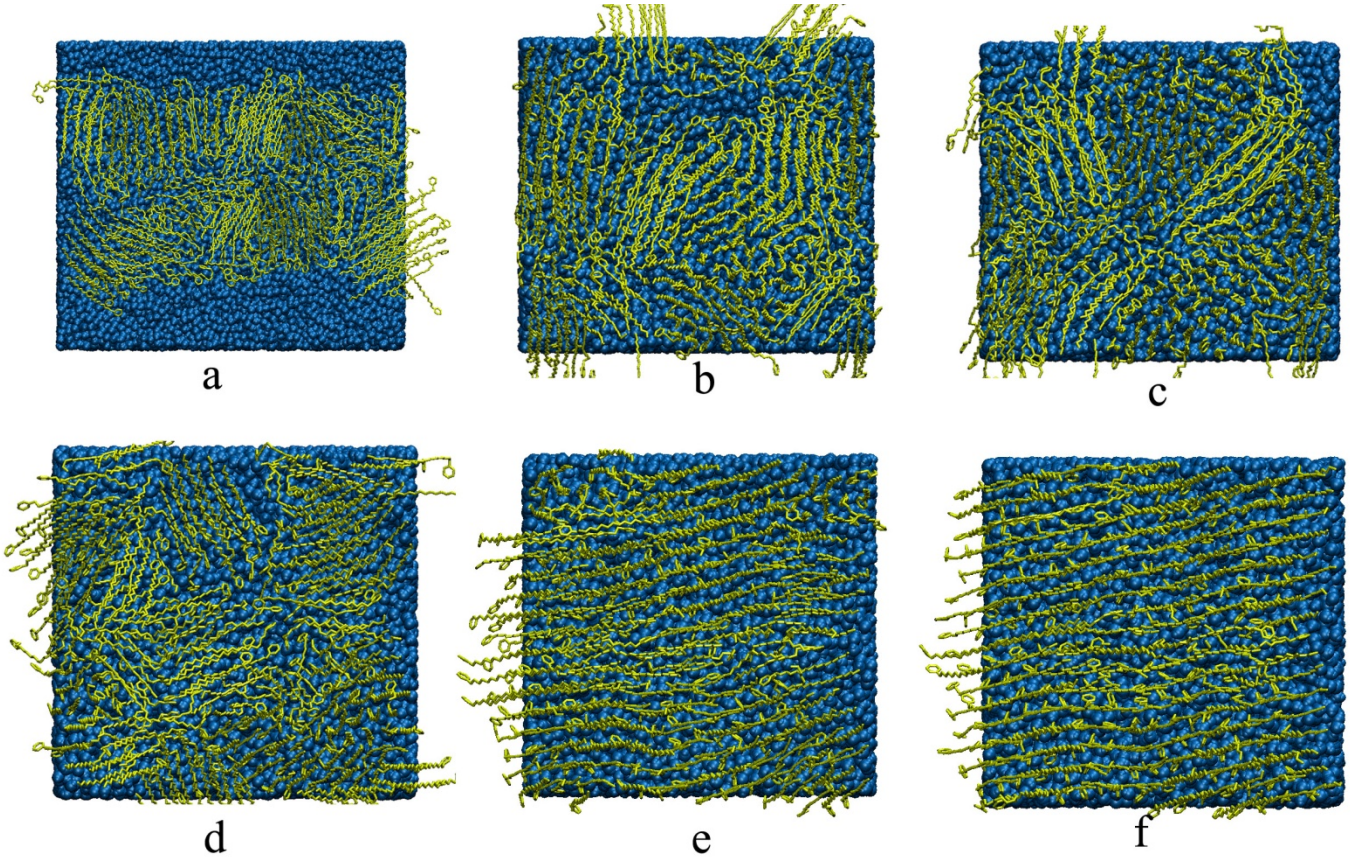


Figure S2 Density profile for ST/water system at 30.5 mN/m. The red line is the curve fitting result. It should be noted that the two peaks at both sides are attributed to part of the organic monolayers on water surface. Since these peaks only occupy a small part of the whole surface, they are not considered during the curve fitting (red line) and the subsequent tail correction.

Tail correction results. For pure water SPC force field γ_{water} (tail)=5.2 mN/m. For TIP4P_2005 force field γ_{water} (tail)=4.3 mN/m:

SPC Force Field			TIP4P_2005 Force Field		
γ (mN/m)	γ_{DOPA_tail} (mN/m)	γ_{ST_tail} (mN/m)	γ (mN/m)	γ_{DOPA_tail} (mN/m)	γ_{ST_tail} (mN/m)
1.5	3.5	3.9	0.2	2.8	4.0
4.0	3.5	3.9	7.7	2.8	4.0
11.5	3.5	3.9	15.2	3.0	4.0
19.0	3.6	3.9	22.7	2.8	4.0
26.5	3.6	3.9	30.2	2.8	4.0
34.0	3.9	3.9	37.7	2.9	4.0
41.5	3.9	3.9	45.2	2.9	4.0
49.0	2.4	3.9	52.7	3.2	4.0
52.8	2.8	3.9	60.2	3.2	4.0
56.5	1.5	3.9	67.7	2.9	3.9
64.0	2.8	3.9			



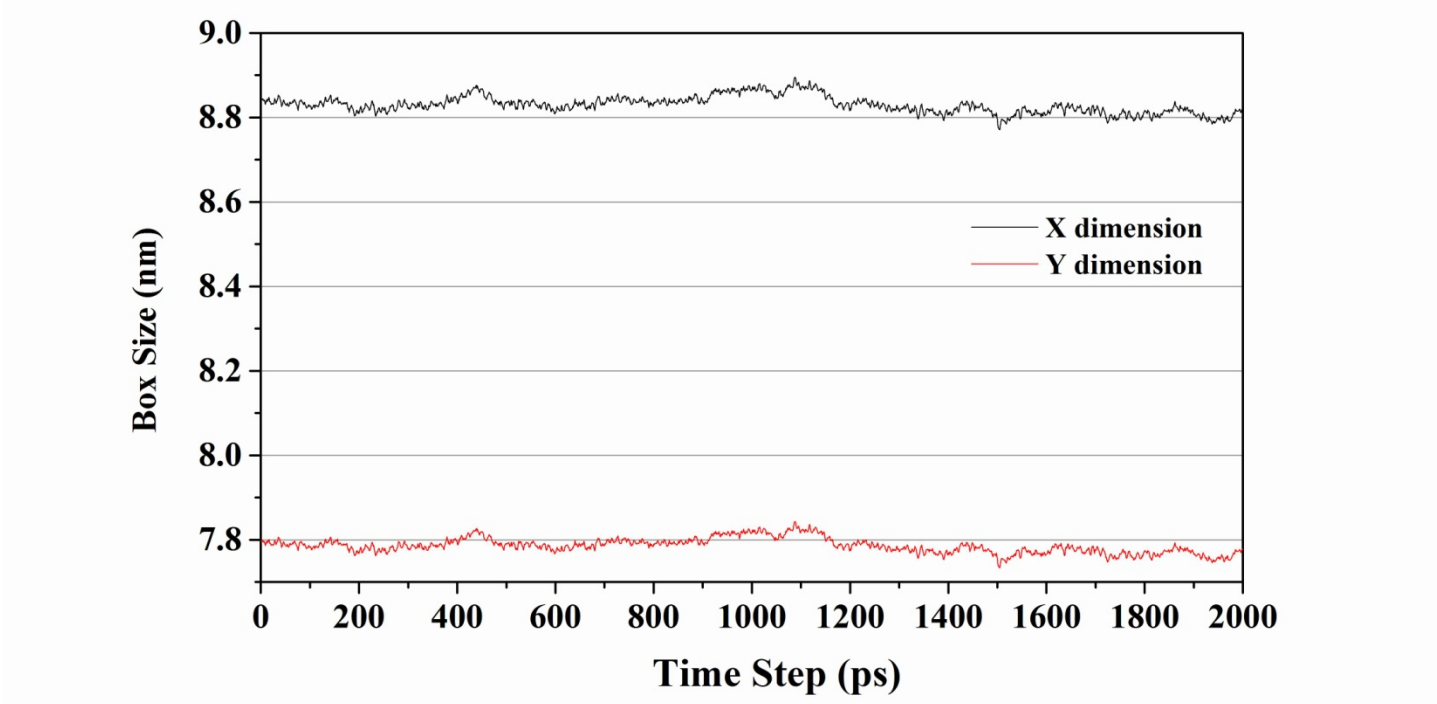


Figure S3 Upper figure: A top view of compression process. a-e are chosen from the different surface pressure steps of MD simulation during ST monolayer compressing. The system is considered equilibrated when the box size in x and y dimensions no longer change. Lower figure: An example of x and y dimension vibrations at an equilibrated state with a surface pressure of 46.6 mN/m for DOPA_large_system.

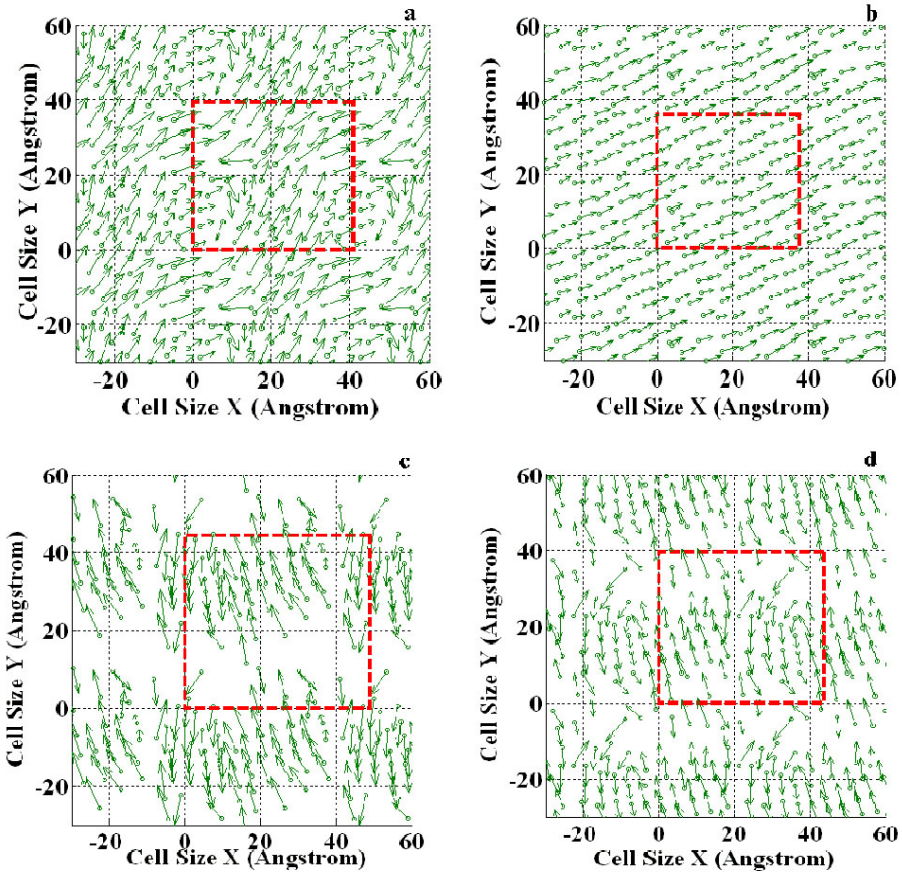


Figure S4 Top view of Vector R_e for small size systems. The red line indicates one cell size. The arrow points from C1 to C17 (Figure 1).(a) ST (surface tension=0.5 mN/m); (b) ST (surface tension=60.5mN/m); (c) DOPA (surface tension=1.6 mN/m); (d) DOPA (surface tension=61.0 mN/m). These result illustrate the artificial boundary conditions when small system size has been applied for simulating linear molecules.

Table S1 Hydrogen bonds between organic molecules and water with different water models

DOPA (Tip4p_2005)				ST (Tip4p_2005)	
π (mN/m)	#amide-Water	# Hydroxyl- water	# Total	π (mN/m)	# Total
1.6	259	1184	1443	0.5	1174
24.2	191	1108	1299	23.0	1098
46.6	133	1074	1207	45.5	1147
61.0	117	1056	1173	60.5	1172

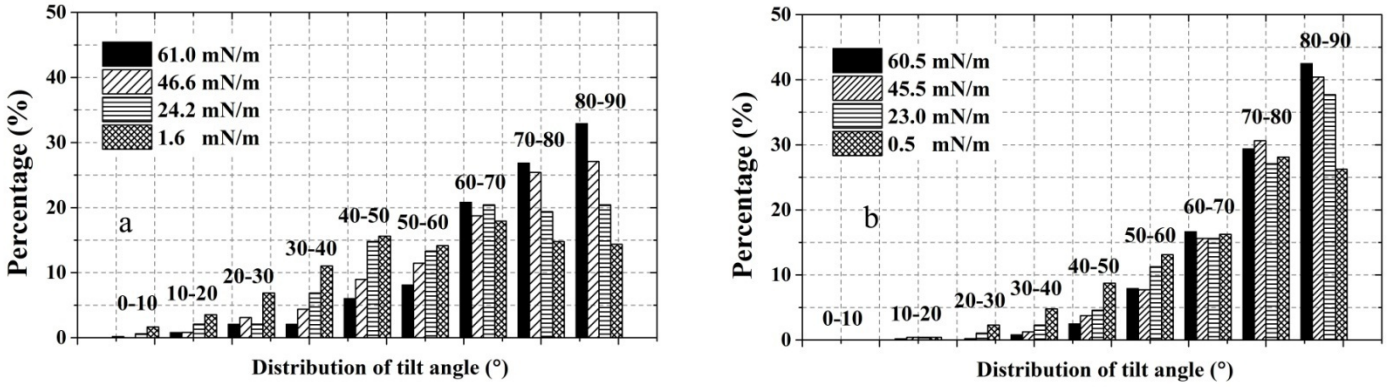
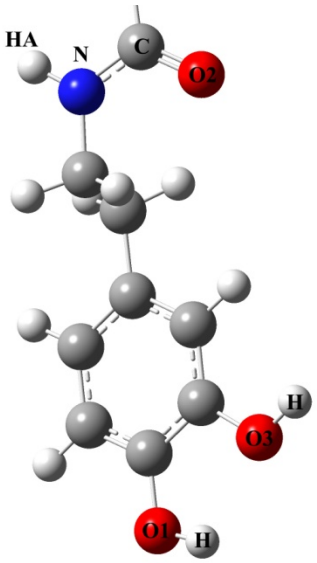


Figure S5 Dihedral angles between aromatic rings and xy-plane, θ distribution for DOPA (a) and ST (b) molecules.



Type 1: N-H···O2 and N-H···N

Type 2: O1/O3-H···O2, N-H···O1/O3, and O1/O3-H···N

Type 3: O1/O3-H···O1/O3

Figure S6 Illustration of hydrogen bond types in DOPA and ST. Type1 is hydrogen bonds between two amide groups; Type 2 is hydrogen bonds between an amide group and a hydroxyl; Type 3 is hydrogen bonds between two hydroxyls.

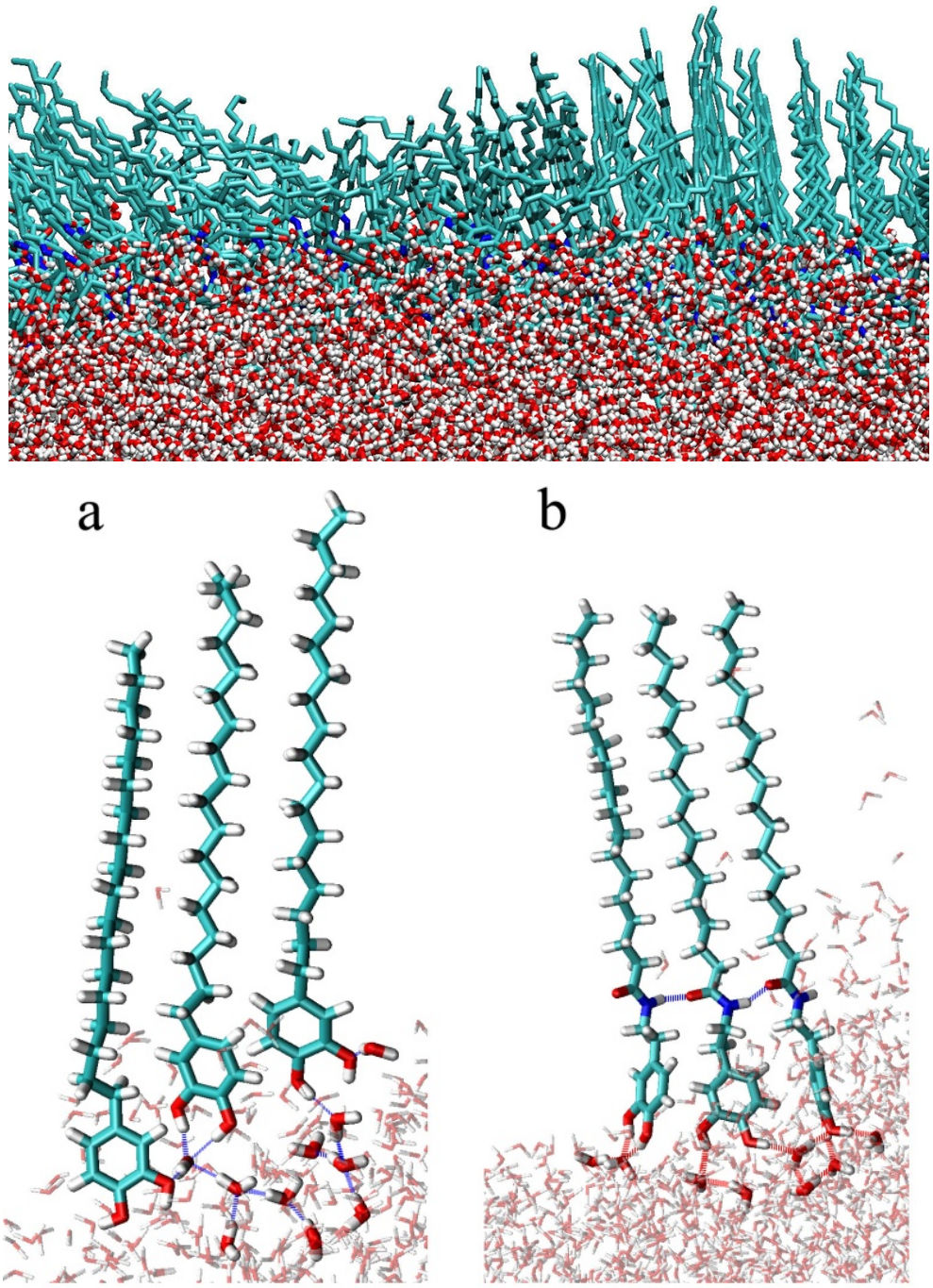


Figure S7 Illustration of a DOPA monolayer on water surface (upper) and illustration of hydrogen bonds in ST at 60.5 mN/m (a) and DOPA at 61.0 mN/m (b).