Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information for: Molecular Dynamics Simulations of Amino Acid Adsorption and Transport at Acetonitrile-Water-Silica Interface: the Role of Side Chains

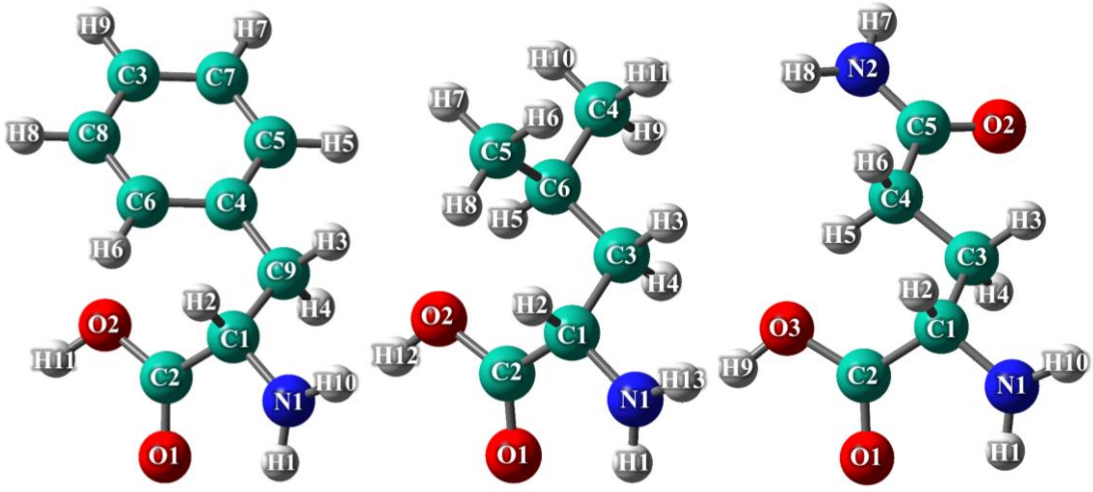
*Yong-Peng Wang, Fei Liang and Shule Liu**

School of Materials Science and Engineering and Key Laboratory for Polymeric

Composite & Functional Materials of Ministry of Education, Sun Yat-sen University,

Guangzhou 510275, P. R. China

Email: liushle@mail.sysu.edu.cn



Phe Leu Gln

Figure S1. The schematic diagram of amino acid molecules with number labels used in Table S1, S2 and S3 as well as in the definition of intramolecular vectors in Fig. 1a of the manuscript.

Table S1. Nonbonding Force Field Parameters for Phe[1]

Phenylalanine (Phe)			
Atom	$q(e_0)$	$\varepsilon_{LJ}(kcal/mol)$	σ_{LJ}(Å)
N1	-0.9038	0.1700	3.25000
O1	-0.5480	0.2100	2.95992
O2	-0.6041	0.2104	3.06647
C1	0.1325	0.1094	3.39967
C2	0.6401	0.0860	3.39967
C3	-0.1280	0.0860	3.39967
C4	-0.0903	0.0860	3.39967
C5	-0.1270	0.0860	3.39967
C6	-0.1270	0.0860	3.39967
C7	-0.1265	0.0860	3.39967
C8	-0.1265	0.0860	3.39967
C9	-0.0721	0.1094	3.39967
H1	0.3658	0.0157	1.06908
H2	0.1037	0.0157	2.47135
H3	0.0627	0.0157	2.64953
H4	0.0627	0.0157	2.64953
H5	0.1375	0.0150	2.59964
H6	0.1375	0.0150	2.59964
H7	0.1330	0.0150	2.59964
H8	0.1330	0.0150	2.59964
H9	0.1330	0.0150	2.59964
H10	0.3658	0.0157	1.06908
H11	0.4460	0.0000	0.00000

Table S2. Nonbonding Force Field Parameters for Leu[1]

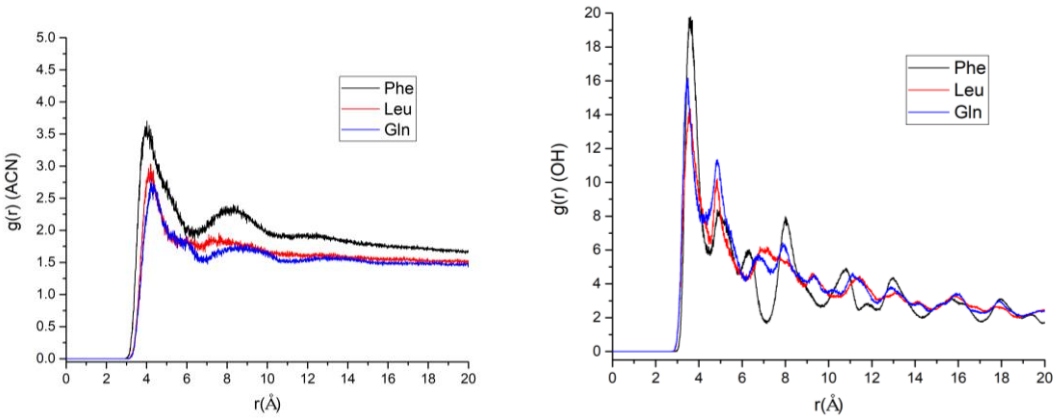
Leucine (Leu)			
Atom	$q(e_0)$	$\varepsilon_{LJ}(kcal/mol)$	σ_{LJ}(Å)
N1	-0.9028	0.1700	3.25000
O1	-0.5510	0.2100	2.95992
O2	-0.6021	0.2104	3.06647
C1	0.1285	0.1094	3.39967
C2	0.6411	0.0860	3.39967
C3	-0.1154	0.1094	3.39967
C4	-0.0911	0.1094	3.39967
C5	-0.0911	0.1094	3.39967
C6	-0.0707	0.1094	3.39967
H1	0.3638	0.0157	1.06908
H2	0.0957	0.0157	2.47135
H3	0.0552	0.0157	2.64953
H4	0.0552	0.0157	2.64953
H5	0.0597	0.0157	2.64953
H6	0.036533	0.0157	2.64953
H7	0.036533	0.0157	2.64953
H8	0.036533	0.0157	2.64953
H9	0.036533	0.0157	2.64953
H10	0.036533	0.0157	2.64953
H11	0.036533	0.0157	2.64953
H12	0.4440	0.0000	0.00000
H13	0.3638	0.0157	1.06908

Table S3. Nonbonding Force Field Parameters for Gln[1]

Glutamine (Gln)			
Atom	$q(e_0)$	$\varepsilon_{LJ}(kcal/mol)$	σ_{LJ}(Å)
N1	-0.9018	0.1700	3.25000
N2	-0.6780	0.1700	3.25000
O1	-0.5420	0.2100	2.95992
O2	-0.6141	0.2100	2.95992
O3	-0.6101	0.2104	3.06647
C1	0.1315	0.1094	3.39967
C2	0.6361	0.0860	3.39967
C3	-0.1124	0.1094	3.39967
C4	-0.1524	0.1094	3.39967
C5	0.6571	0.0860	3.39967
H1	0.3673	0.0157	1.06908
H2	0.0917	0.0157	2.47135
H3	0.0737	0.0157	2.64953
H4	0.0737	0.0157	2.64953
H5	0.0702	0.0157	2.64953
H6	0.0702	0.0157	2.64953
H7	0.3125	0.0157	1.06908
H8	0.3125	0.0157	1.06908
H9	0.4460	0.0000	0.00000
H10	0.3673	0.0157	1.06908

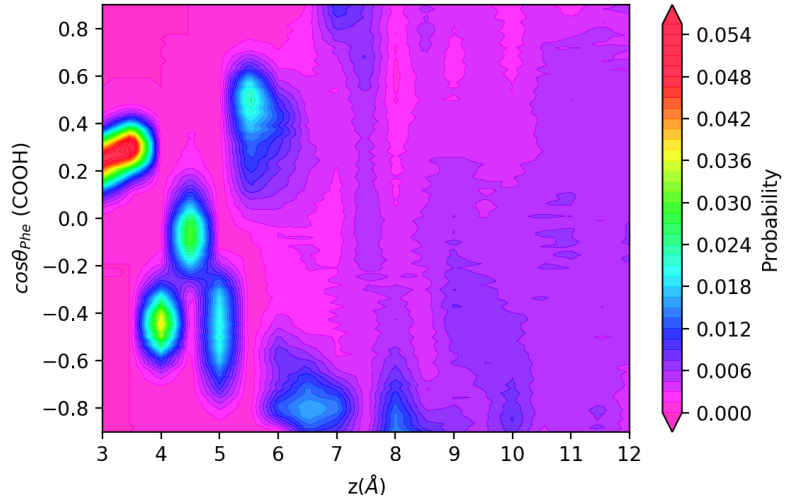
Table S4. Nonbonding Force Field Parameters for ACN[2], Water[3] and Silica[4]

Molecule	Atom	$q(e_0)$	$\varepsilon_{LJ}(kcal/mol)$	σ_{LJ}(Å)
ACN	N (ACN)	-0.5126	0.1331	3.0112
	C (cyano)	0.4617	0.1341	3.5458
	C (methyl)	-0.5503	0.1094	3.3997
	H (ACN)	0.1904	0.0157	2.6495
water	O (water)	-0.8340	0.1521	3.1506
	H (water)	0.4170	0.0000	0.0000
silica	H (Silanol)	0.4000	0.0000	0.0000
	O (Silanol)	-0.7100	0.1550	3.1540
	Si (Silanol)	0.3100	0.1275	3.7950
	O (wall)	0.0000	0.1550	3.1540
	Si (wall)	0.0000	0.1275	3.7950

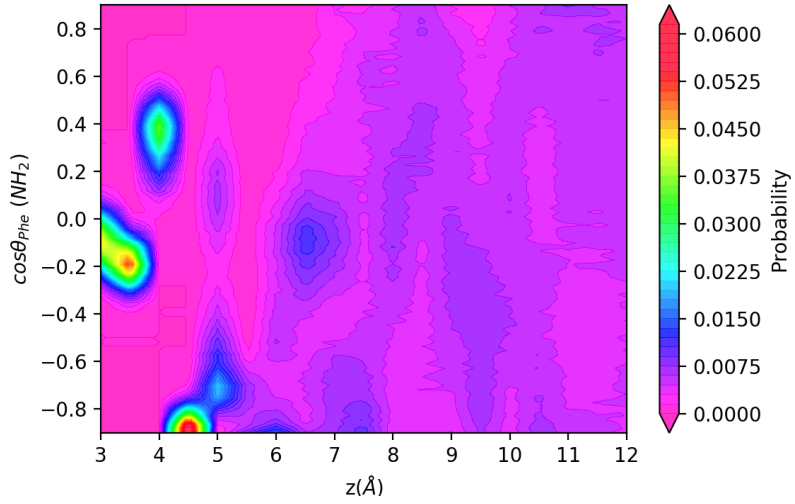


(a) (b)

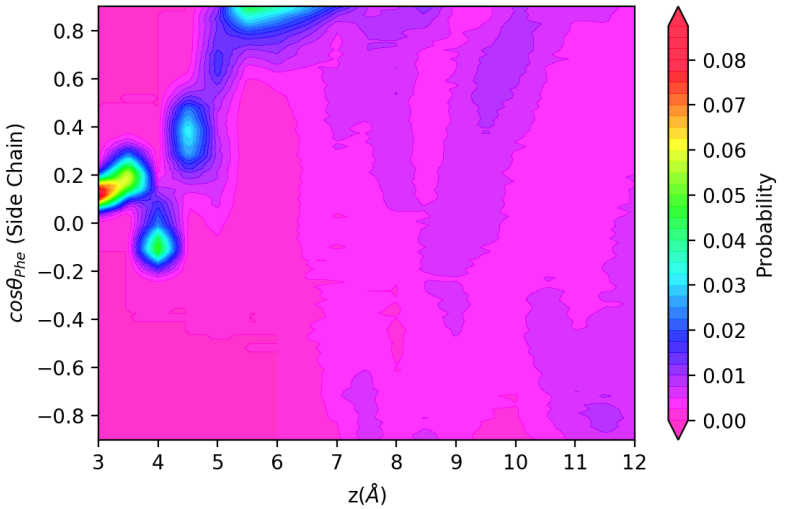
Figure S2. (a) The radial distribution function of ACN at the most stabilized state of each amino acid as the function of the distance between the β-C atom of each amino acid and methyl carbon atoms from ACN molecules. (b) The radial distribution function of hydroxyl groups in solvent system (water molecules and silanol groups) at the most stabilized state of each amino acid as the distance between the α-C atom of each amino acids and oxygen atoms of hydroxyl groups.


0.8
0.6
0.4
0.2
0.0
−0.2
−0.4
−0.6
−0.8
$cos\theta_{Phe}$ (COOH)
3
4
5
6
7
8
9
10
11
12
z(Å)
0.054
0.048
0.042
0.036
0.030
0.024
0.018
0.012
0.006
0.000
Probability

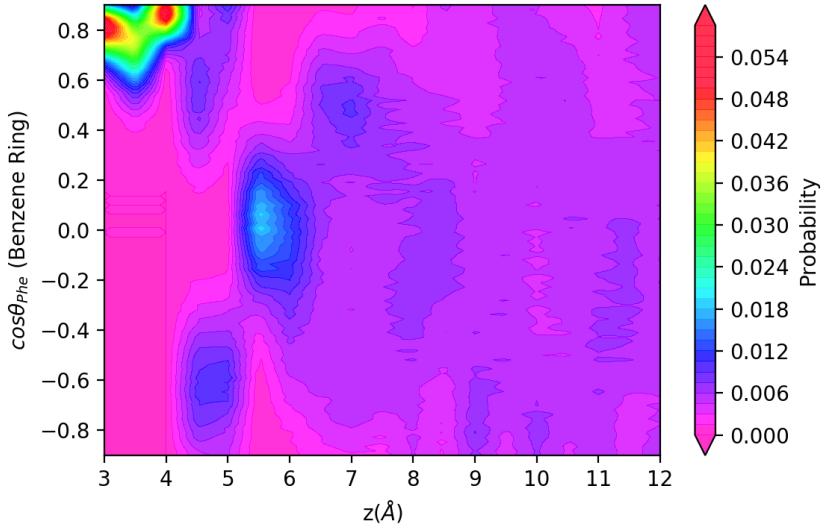
(a)


0.8
0.6
0.4
0.2
0.0
−0.2
−0.4
−0.6
−0.8
$cos\theta_{Phe}$ (NH_2)
3
4
5
6
7
8
9
10
11
12
z(Å)
0.0600
0.0525
0.0450
0.0375
0.0300
0.0225
0.0150
0.0075
0.0000
Probability

(b)

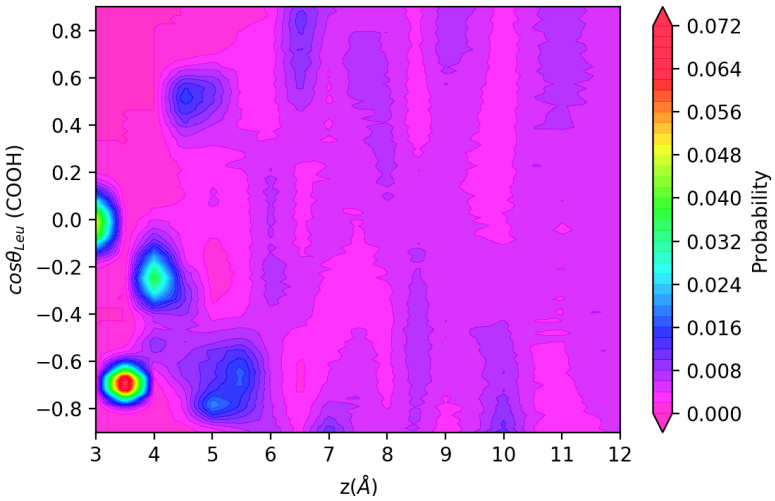

0.8
0.6
0.4
0.2
0.0
−0.2
−0.4
−0.6
−0.8
$cos\theta_{Phe}$ (Side Chain)
3
4
5
6
7
8
9
10
11
12
z(Å)
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
Probability

(c)

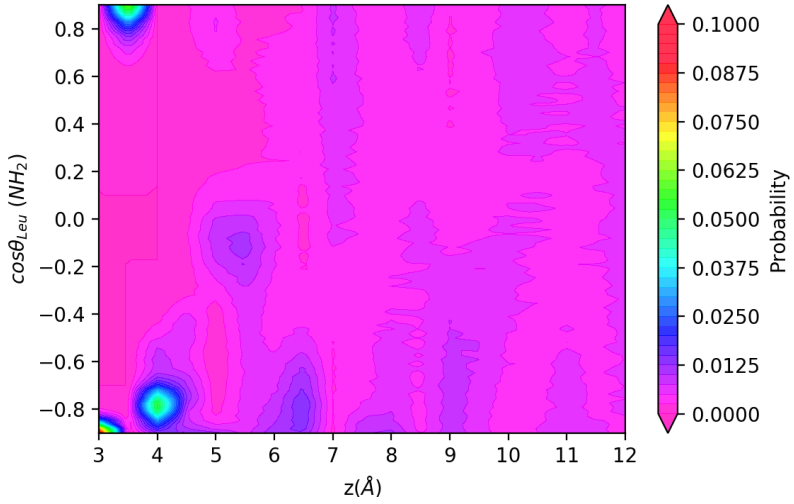


(d)

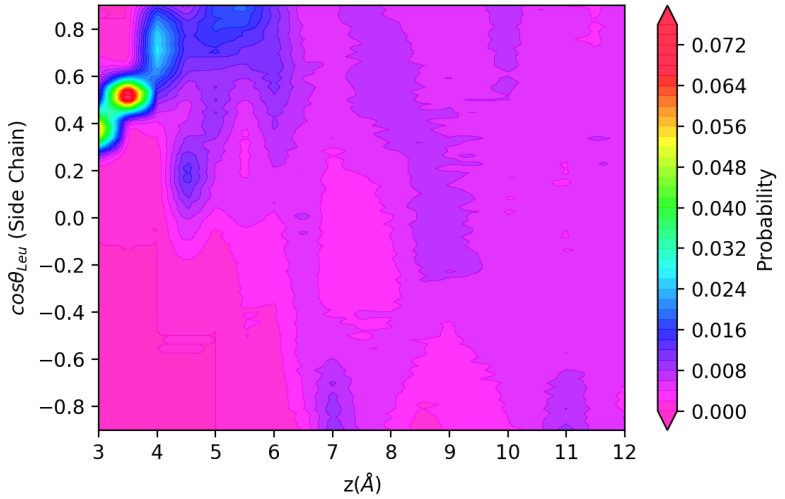
Figure S3. The orientation distribution of the Phe molecule's (a) C_1-C_2 vector: α-carbon atom C_1 pointing towards the C_2 atom of the carboxyl group, (b) C_1-N_1vector: α-carbon atom C_1 pointing towards the N_1 atom of the amino group, (c) C_1-C_3 vector: α-carbon atom C_1 pointing towards the C_3 atom of phenyl side chain group and (d) the normal vector of the benzene ring as a function of the center-of-mass distance from the silica surface. This figure is plotted by combining the corresponding orientation distribution profiles in all umbrella sampling windows.



(a)

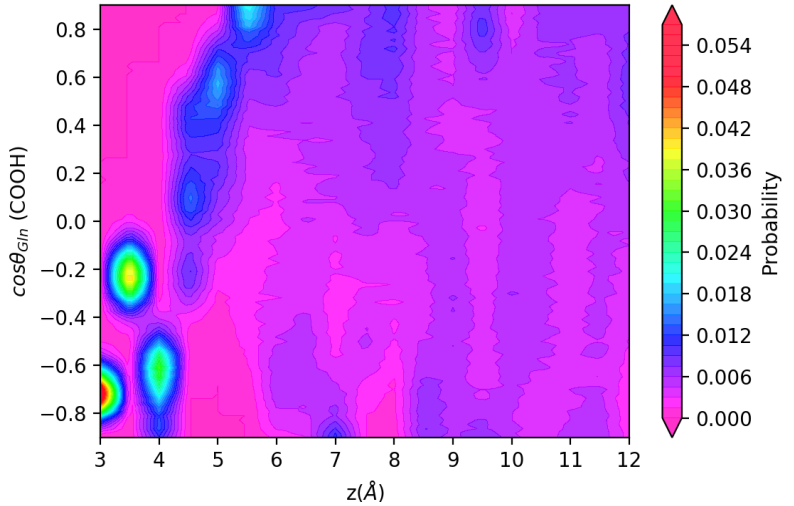


(b)

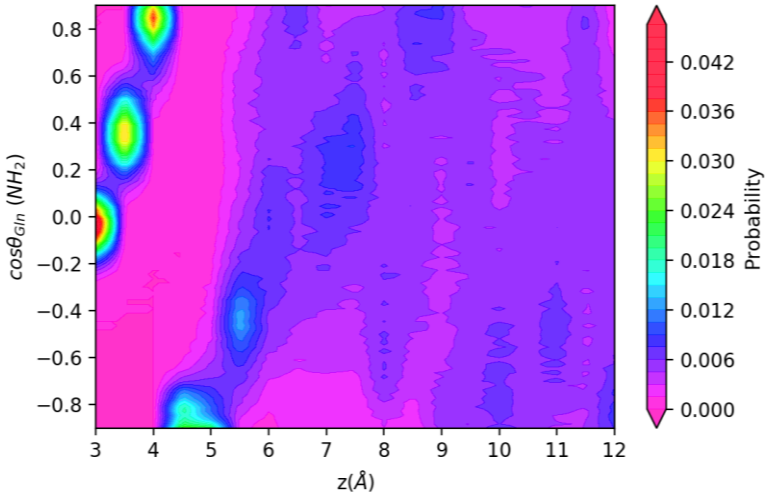


(c)

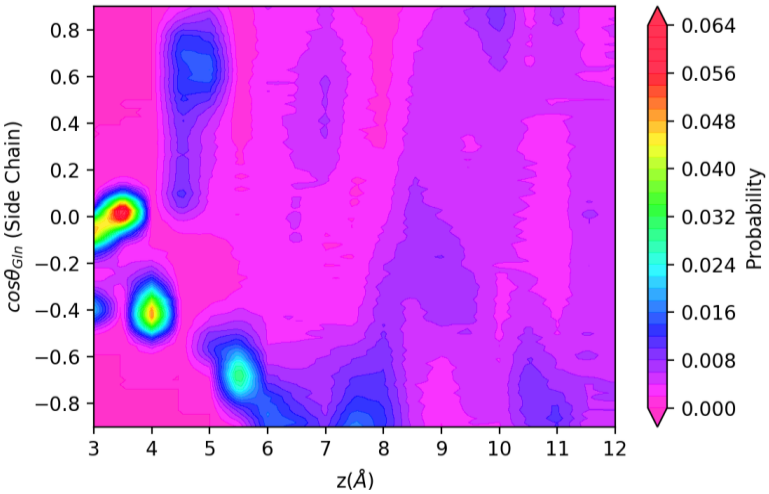
Figure S4. The orientation distribution of the Leu molecule's (a) C_1-C_2 vector: α-carbon atom C_1 pointing towards the C_2 atom of the carboxyl group, (b) C_1-N_1vector: α-carbon atom C_1 pointing towards the N_1 atom of the amino group and (c) C_1-C_4 vector: α-carbon atom C_1 pointing towards the C_4 atom of the isobutyl side chain group as a function of the center-of-mass distance from the silica surface. This figure is plotted by combining the corresponding orientation distribution profiles in all umbrella sampling windows.



(a)



(b)



(c)

Figure S5. The orientation distribution of the Gln molecule's (a) C_1-C_2 vector: α-carbon atom C_1 pointing towards the C_2 atom of the carboxyl group, (b) C_1-N_1vector: α-carbon atom C_1 pointing towards the N_1 atom of the amino group and (c) C_1-N_2 vector: α-carbon atom C_1 pointing towards the N_2 atom of the amide side chain group as a function of the center-of-mass distance from the silica surface. This figure is plotted by combining the corresponding orientation distribution profiles in all umbrella sampling windows.

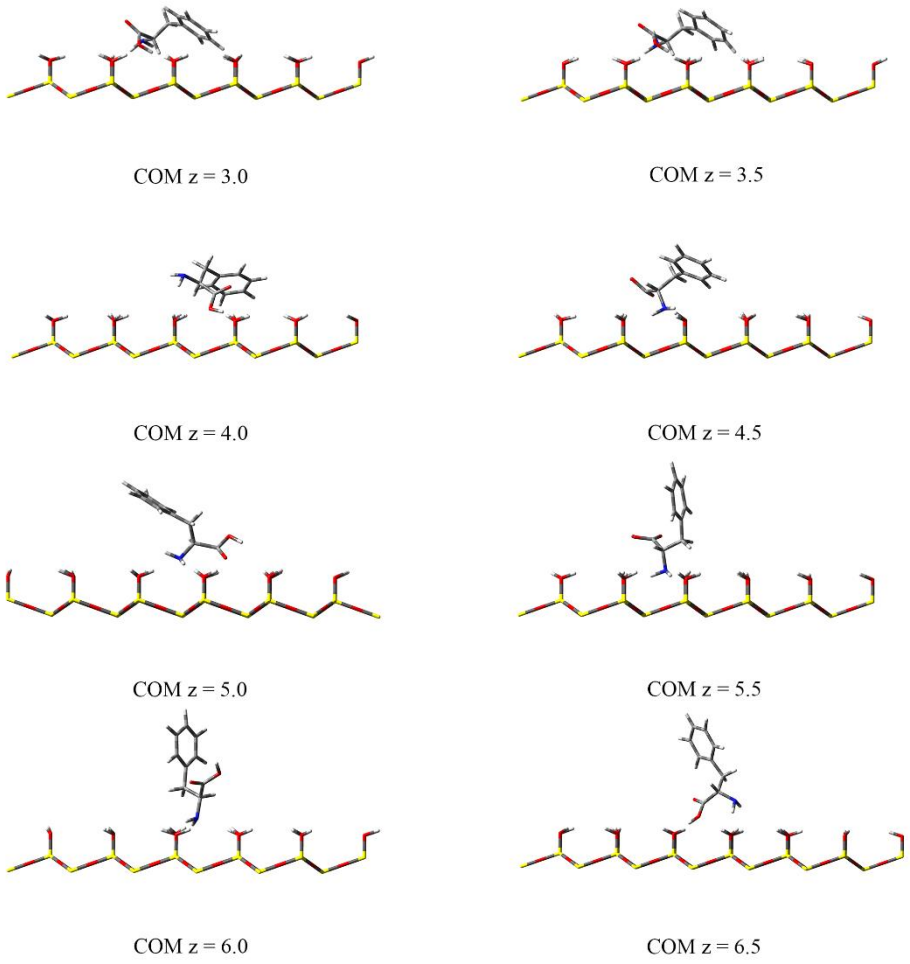


Figure S6. Typical configurations of Phe on the silica surface at the COM z position ranging from z = 3.0 Å to z = 6.5 Å. Acetonitrile (ACN) and water are not shown for clarity.

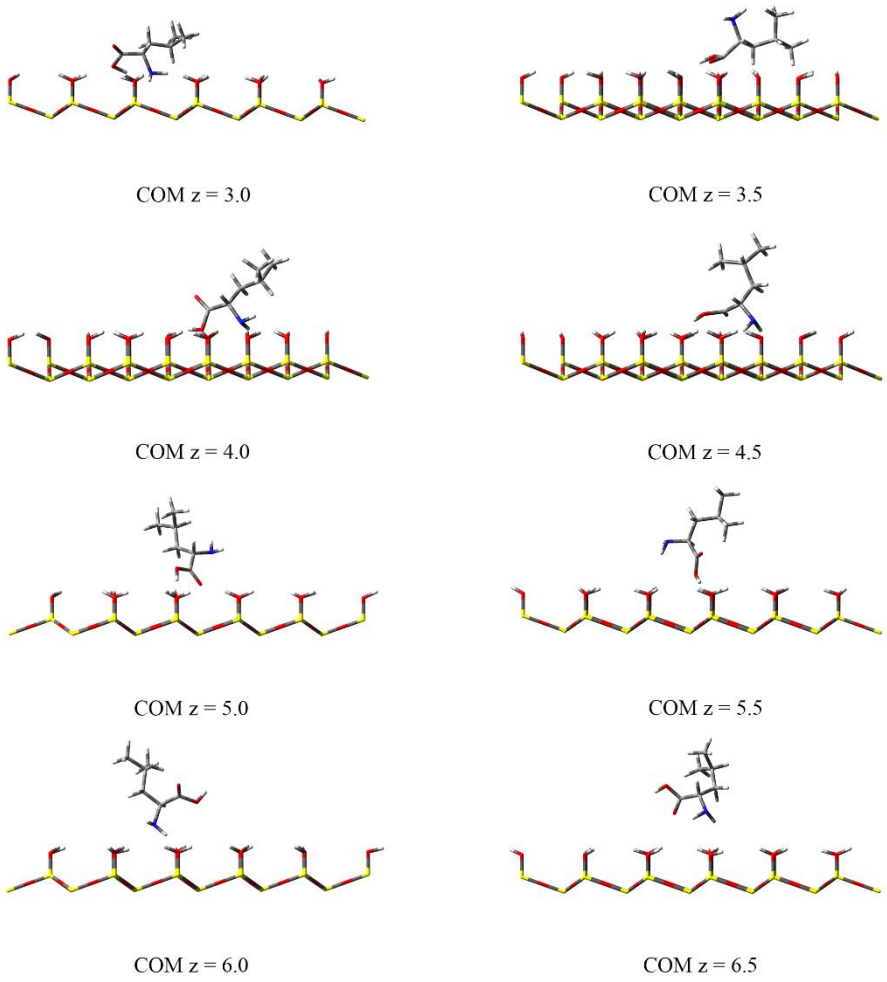


Figure S7. Typical configurations of Leu on the silica surface at the COM z position ranging from z = 3.0 Å to z = 6.5 Å. Acetonitrile (ACN) and water are not shown for clarity.

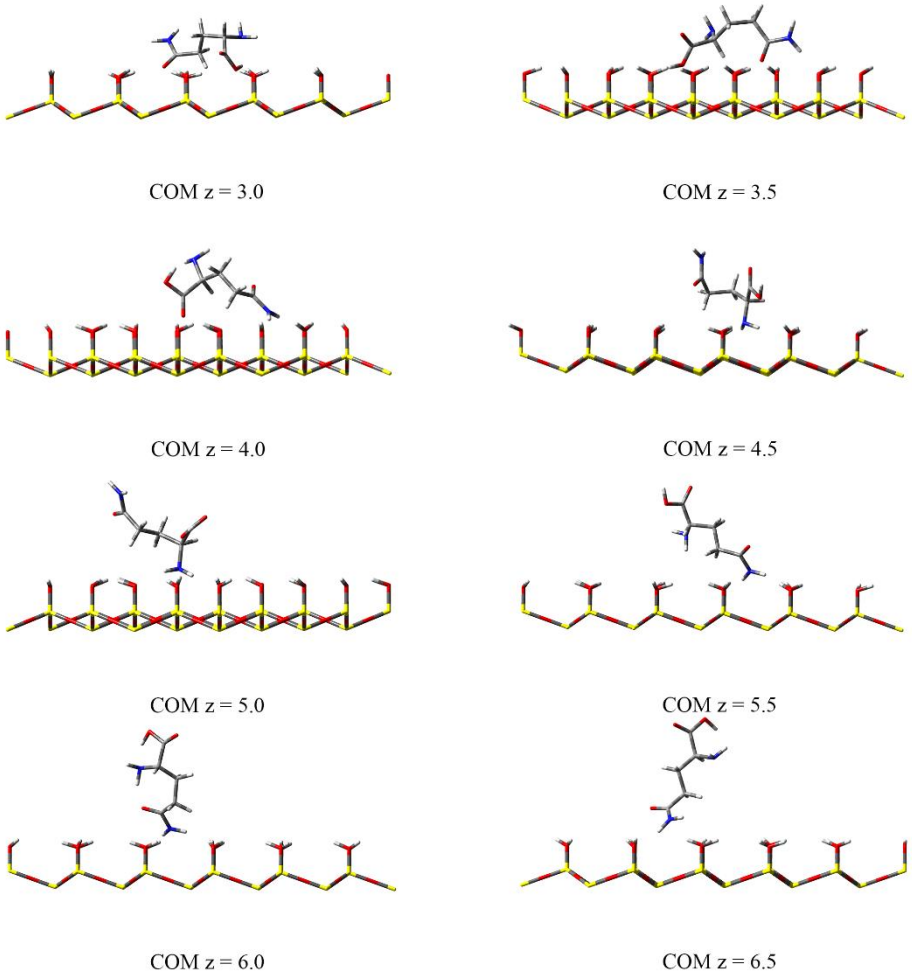


Figure S8. Typical configurations of Gln on the silica surface at the COM z position ranging from z = 3.0 Å to z = 6.5 Å. Acetonitrile (ACN) and water are not shown for clarity.

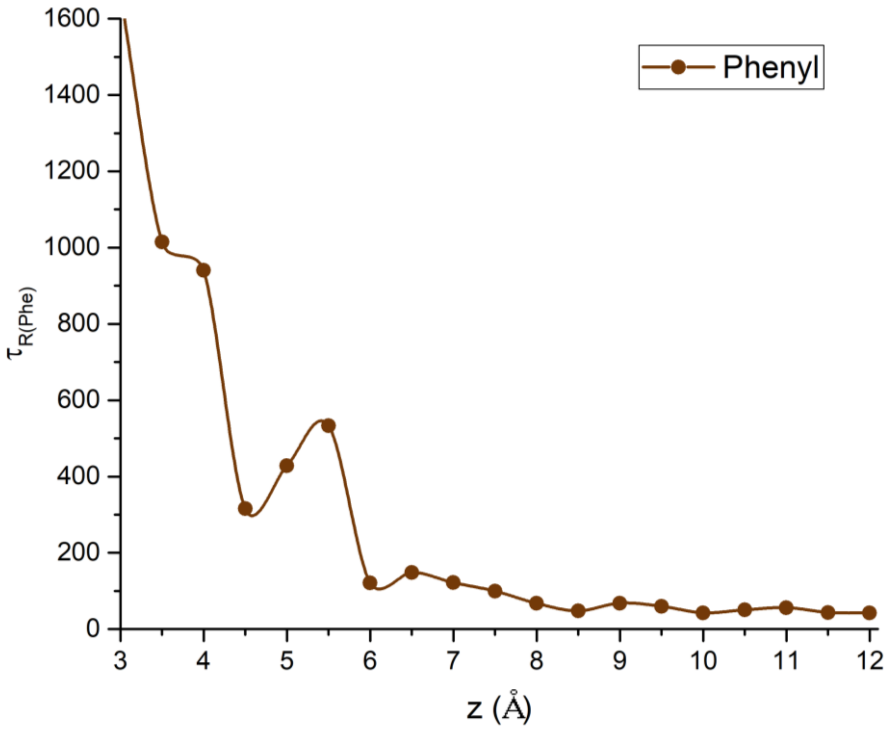
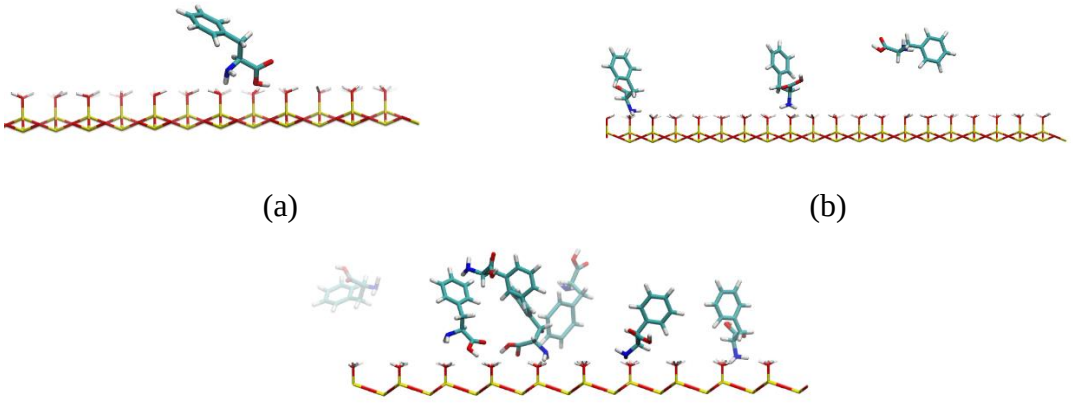


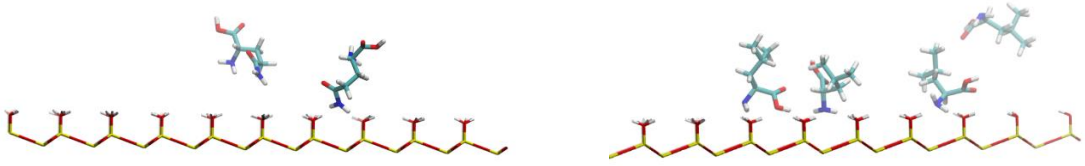
Figure S9. The rotational relaxation time τ curve for the phenyl ring normal vector of the Phe molecule as a function of the z distance from the surface, with the definition of the vector shown in Figure 1a of the manuscript.



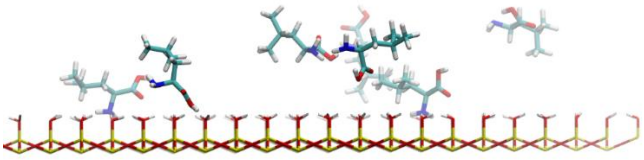
(a) (b)

(c)

Figure S10. Typical configurations of Phe within 8 Å from the silica surface with different number of amino acid molecules (a) 10, (b) 30 and (c) 50.

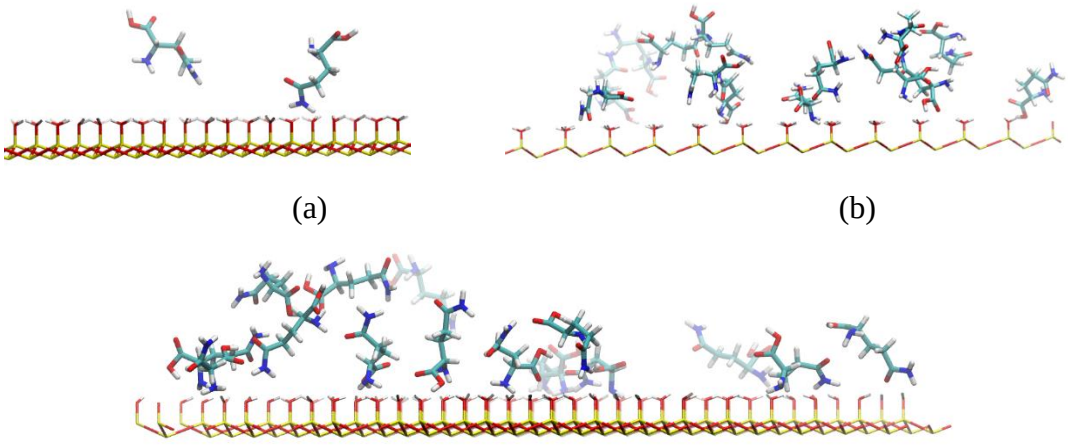


(a) (b)



(c)

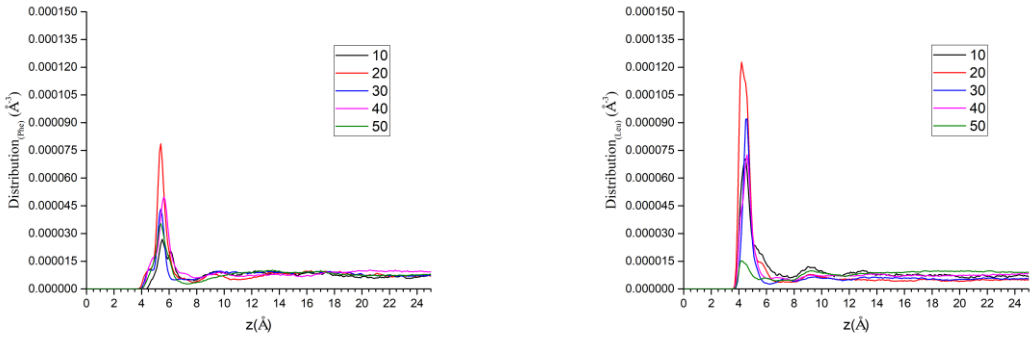
Figure S11. Typical configurations of Leu within 8 Å from the silica surface with different number of amino acid molecules (a) 10, (b) 30 and (c) 50.



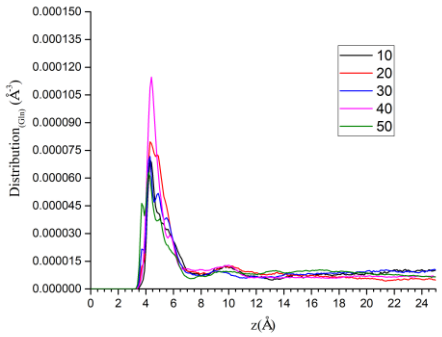
(a) (b)

(c)

Figure S12. Typical configurations of Gln within 8 Å from the silica surface with different number of amino acid molecules (a) 10, (b) 30 and (c) 50.

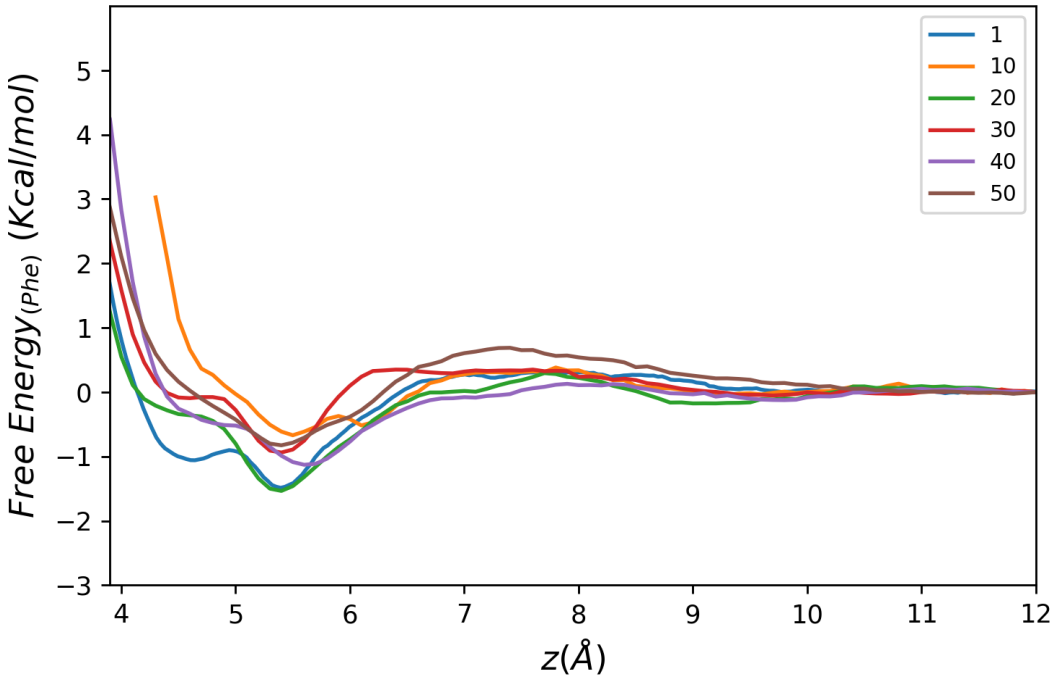


(a) (b)

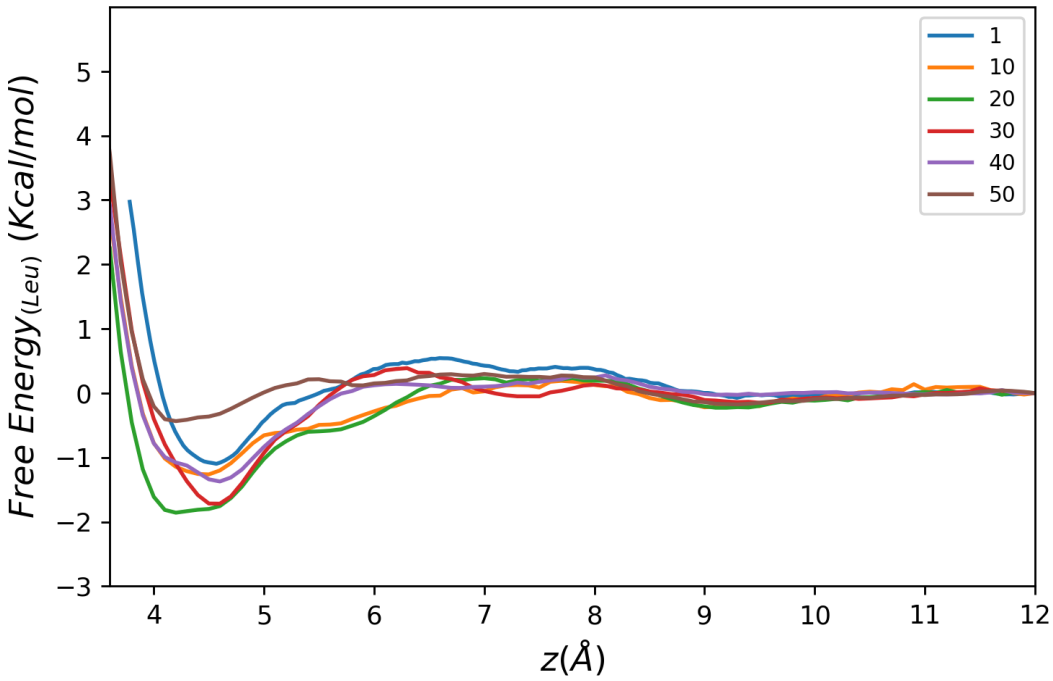


(c)

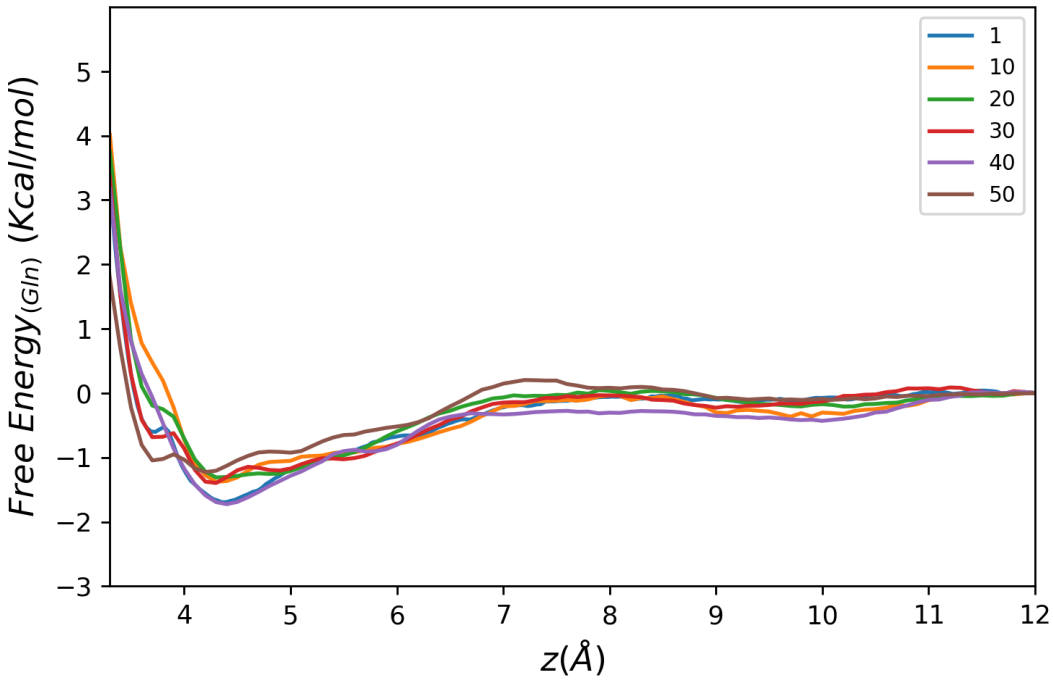
Figure S13. Spatial probability distribution functions of (a) Phe, (b) Leu and (c) Gln with different number of amino acid molecules. The spatial probability distribution is calculated via scaling the number density profiles by the number of amino acid molecules in the system.



(a)



(b)



(c)

Figure S14. PMFs of (a) Phe, (b) Leu and (c) Gln with different number of amino acid molecules.

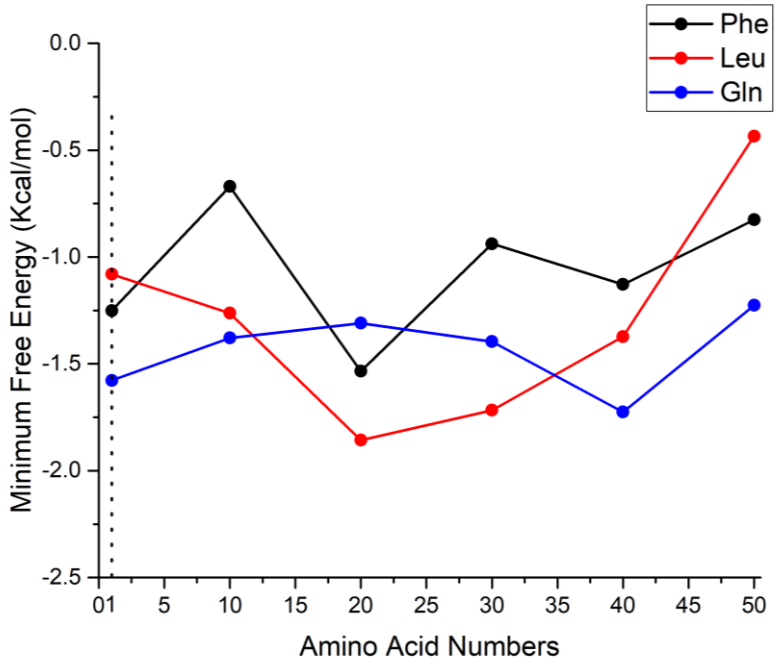


Figure S15. The minimums of the free energy of Phe (black line), Leu (red line) and Gln (blue line) molecules with different number of solute molecules in the water-ACN-silica system.

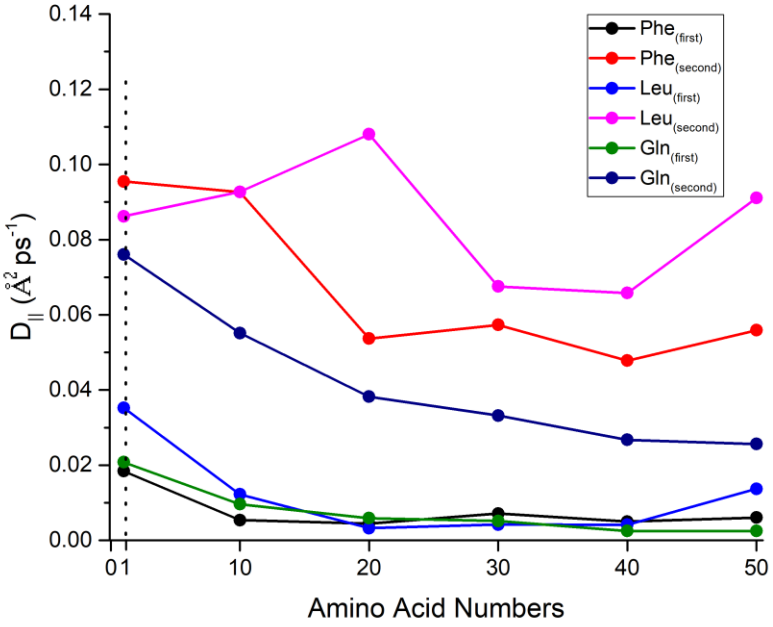


Figure S16. The parallel diffusion coefficients for systems with different number of solute molecules in the first layer (z = 3-7 Å, black line: the Phe molecule, blue line: the Leu molecule and green line: the Gln molecule) and second layer (z = 7-11 Å, red line: the Phe molecule, pink line: the Leu molecule and navy blue line: the Gln molecule).

References

1. Wang, J. M.; Wolf, R. M.; Caldwell, J. W.; Kollman, P. A.; Case, D. A., Development and testing of a general amber force field. *Journal of computational chemistry* **2004,** *25* (9), 1157-1174.

2. Nikitin, A. M.; Lyubartsev, A. P., New six-site acetonitrile model for simulations of liquid acetonitrile and its aqueous mixtures. *Journal of computational chemistry* **2007,** *28* (12), 2020-6.

3. Jorgensen, W. L.; Chandrasekhar, J.; Madura, J. D.; Impey, R. W.; Klein, M. L., Comparison of simple potential functions for simulating liquid water. *J. Chem. Phys.* **1983,** *79* (2), 926-935.

4. Song Hi, L.; Rossky, P. J., A comparison of the structure and dynamics of liquid water at hydrophobic and hydrophilic surfaces-a molecular dynamics simulation study. *J. Chem. Phys.* **1994,** *100* (4), 3334-3345.