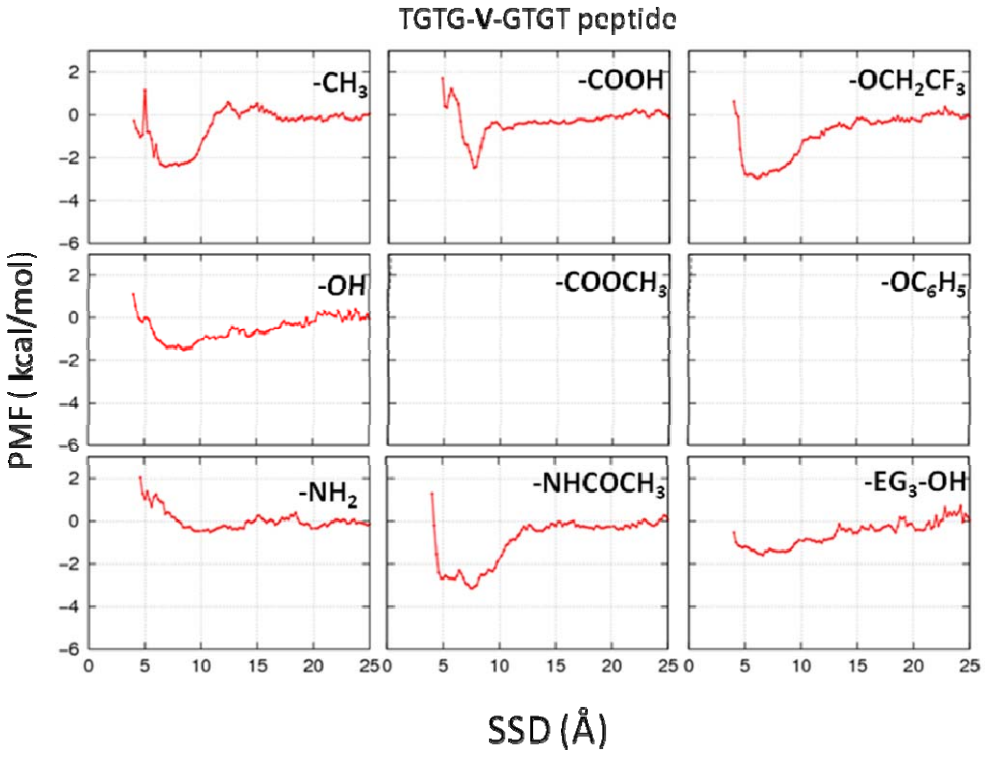
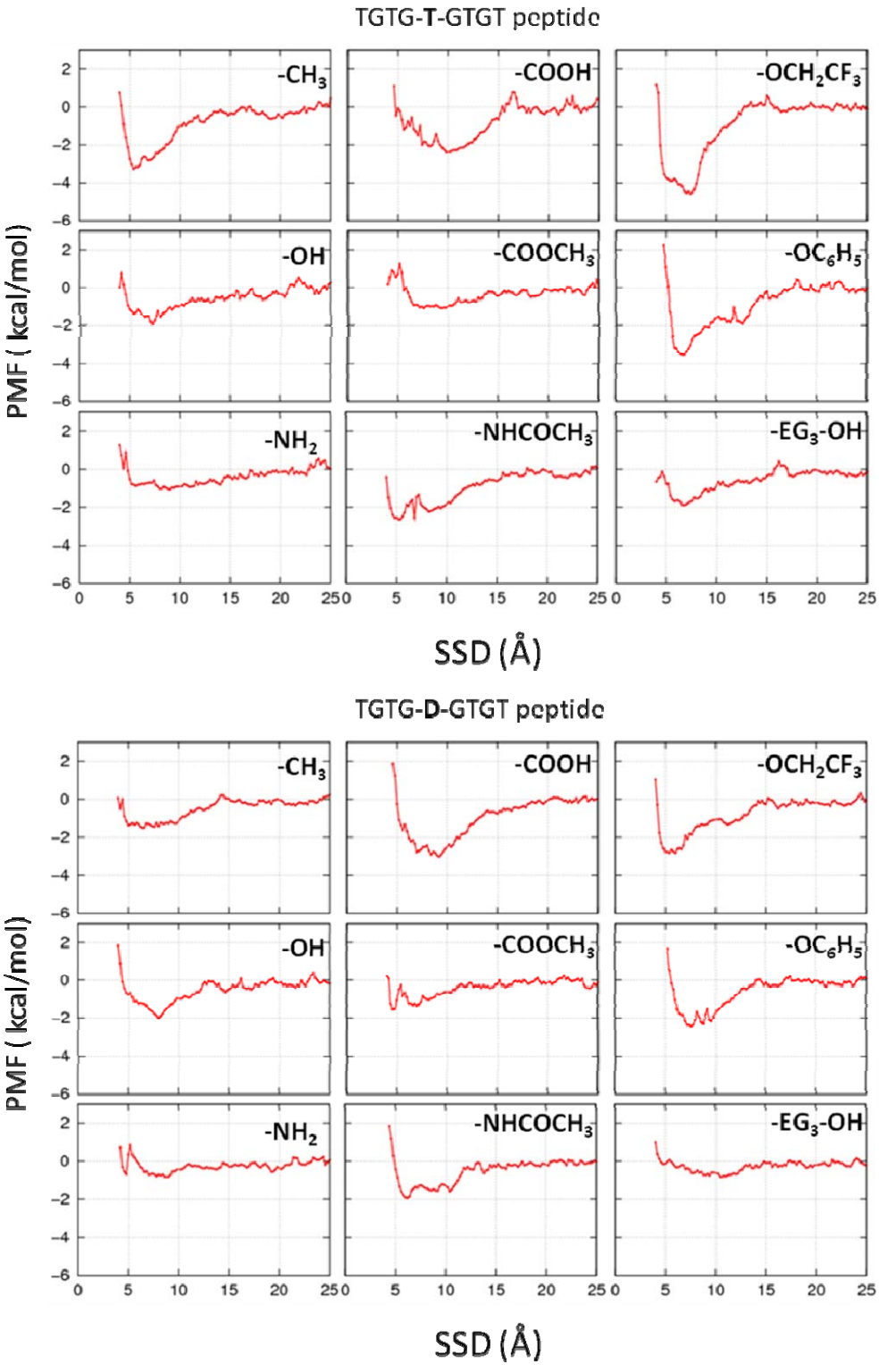
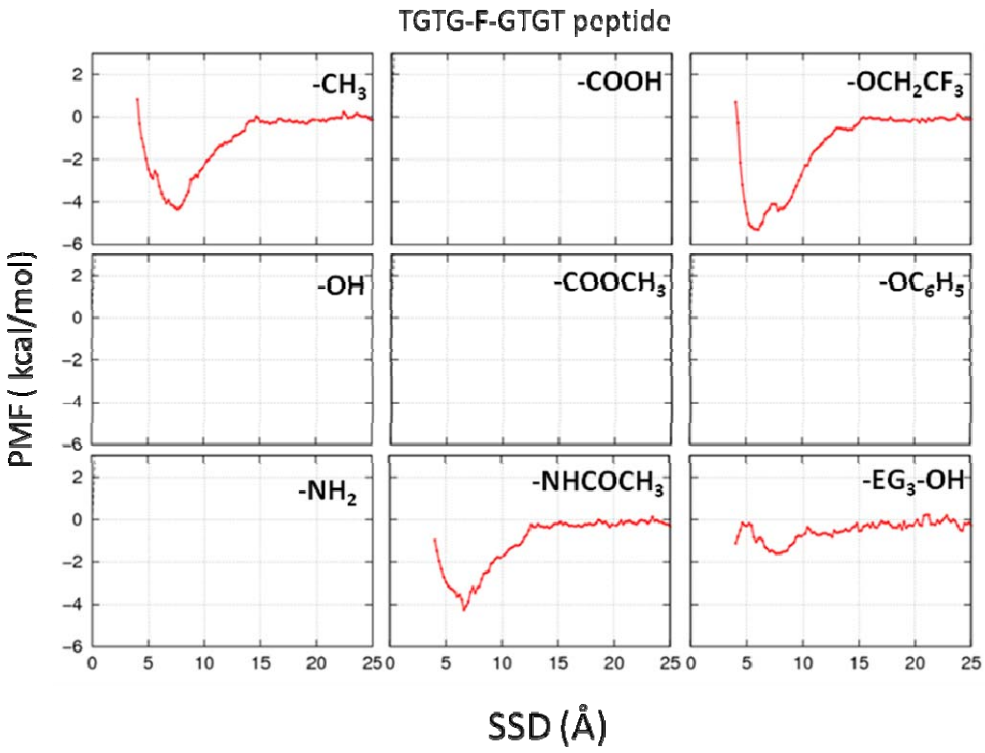
Table S.1: Height of the simulation box considered for nine different SAM surfaces. The base dimensions are 43.30 Å x 45.00 Å.

Alkanethiol SAM	Box Height (Å)
$HS(CH_2)_{11}$-$\mathbf{CH_3}$	64.43
$HS(CH_2)_{11}$-**OH**	62.68
$HS(CH_2)_{11}$-$\mathbf{NH_2/NH_3^+}$	62.67
$HS(CH_2)_{11}$-$\mathbf{COO^-/COOH}$	62.42
$HS(CH_2)_{11}$-$\mathbf{COOCH_3}$	65.56
$HS(CH_2)_{11}$-$\mathbf{NHCOCH_3}$	65.85
$HS(CH_2)_{11}$-$\mathbf{OCH_2CF_3}$	66.78
$HS(CH_2)_{11}$-$\mathbf{OC_6H_5}$	67.37
$HS(CH_2)_{11}$-$\mathbf{(OCH_2CH_2)_3}$-OH	71.63

Figure S.1: Free energy profiles extracted from the 5 – 7 ns REMD simulations for each of the TGTG-X-GTGT peptides over nine different SAM surfaces.




TGTG-T-GTGT peptide
-CH3
-COOH
-OCH2CF3
-OH
-COOCH3
-OC6H5
-NH2
-NHCOCH3
-EG3-OH
PMF (kcal/mol)
SSD (Å)
TGTG-D-GTGT peptide
-CH3
-COOH
-OCH2CF3
-OH
-COOCH3
-OC6H5
-NH2
-NHCOCH3
-EG3-OH
PMF (kcal/mol)
SSD (Å)


TGTG-F-GTGT peptide
-CH3
-COOH
-OCH2CF3
-OH
-COOCH3
-OC6H5
-NH2
-NHCOCH3
-EG3-OH
PMF (kcal/mol)
SSD (Å)

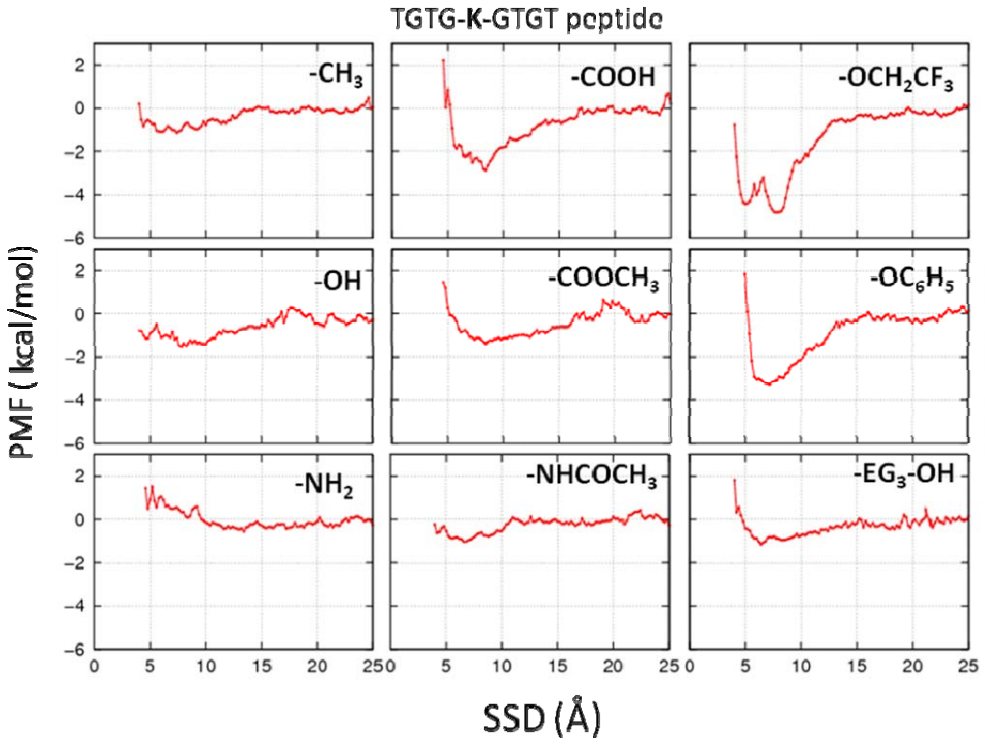
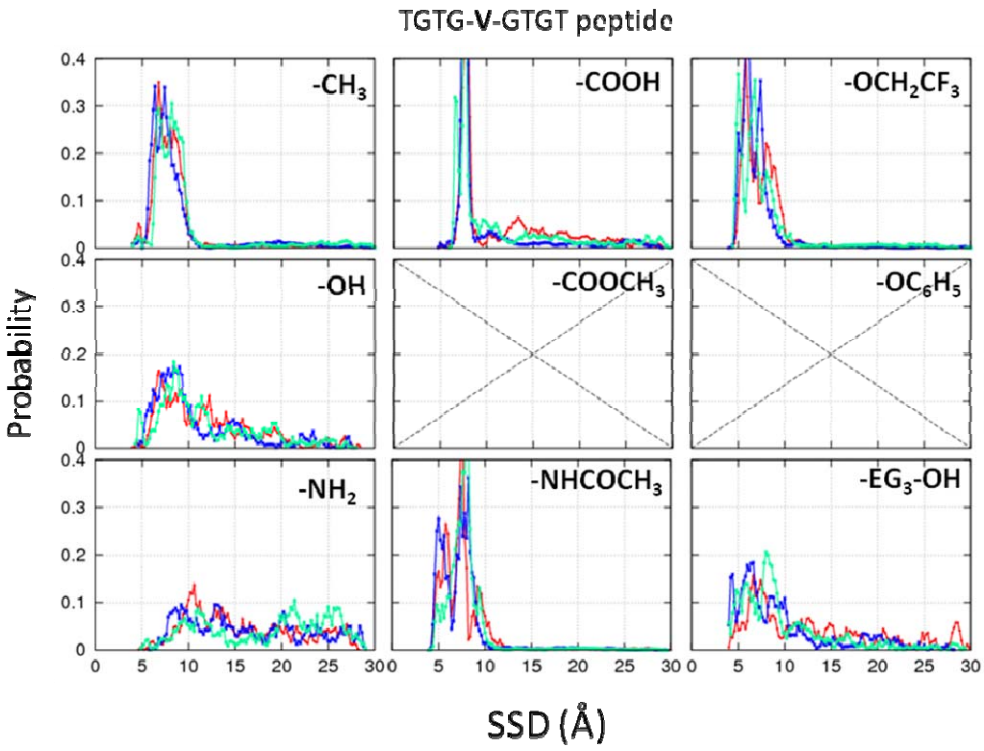
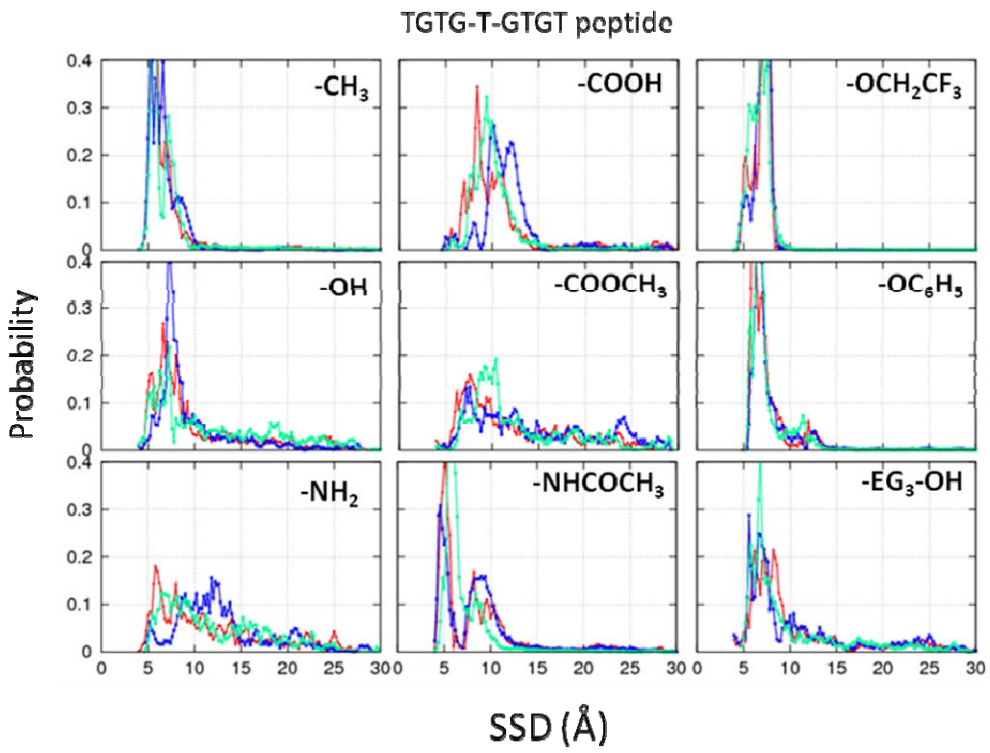
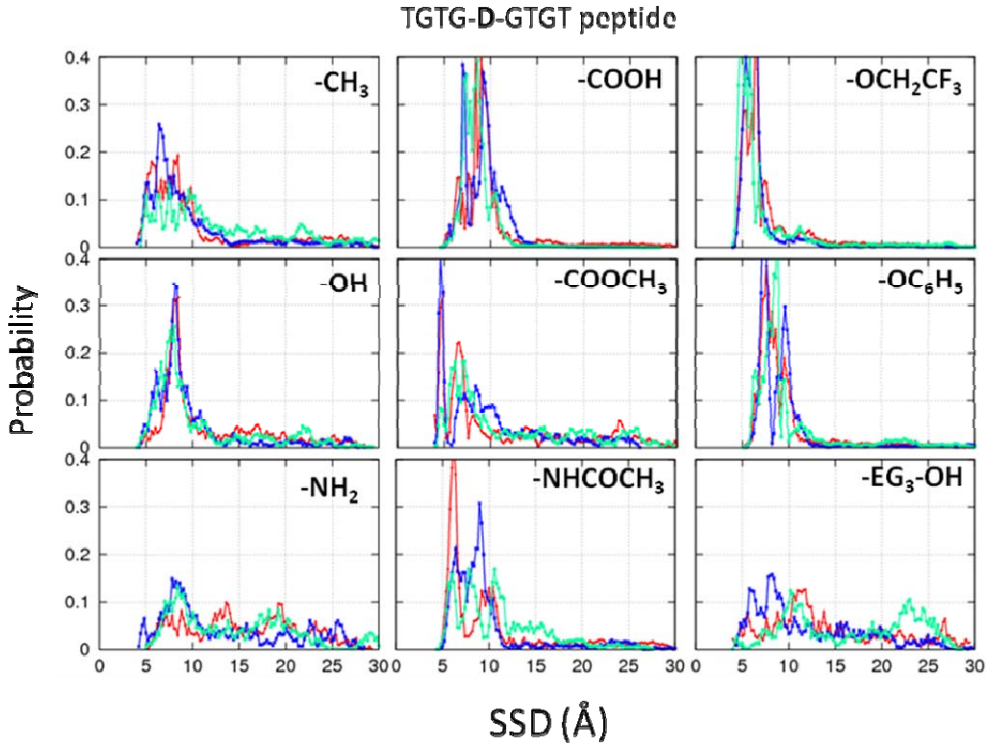
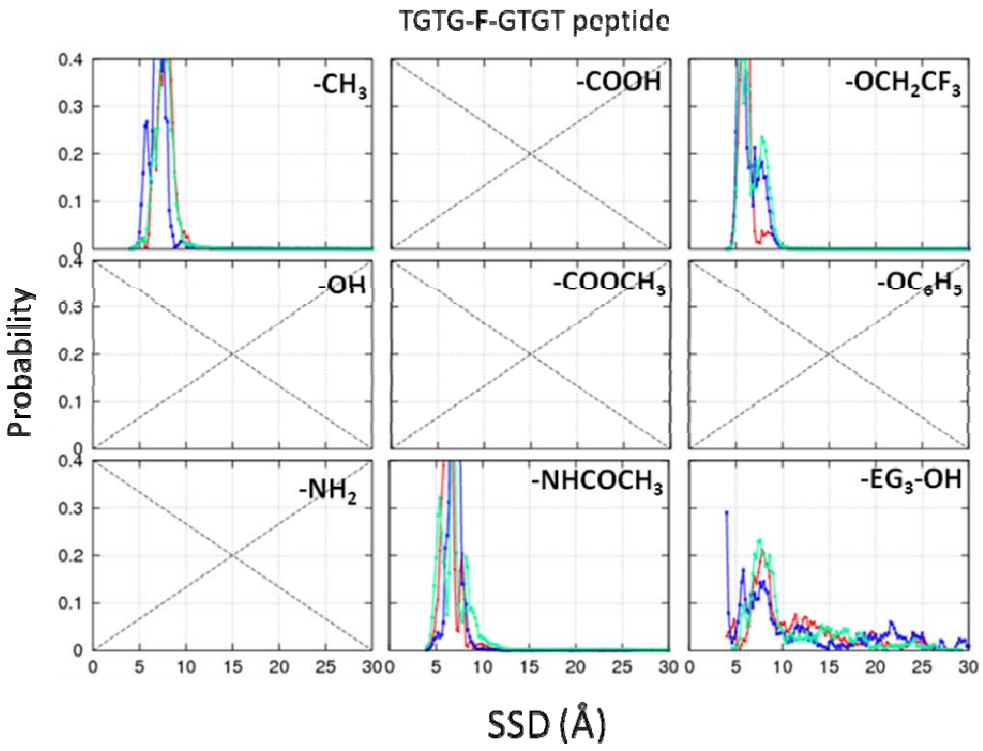

TGTG-K-GTGT peptide
-CH3
-COOH
-OCH2CF3
-OH
-COOCH3
-OC6H5
-NH2
-NHCOCH3
-EG3-OH
PMF (kcal/mol)
SSD (Å)

Figure S.2: Normalized unbiased probability density plots for three independent runs (red, cyan, and blue) from the REMD simulations for each of the TGTG-X-GTGT peptides over nine different SAM surfaces.




TGTG-T-GTGT peptide
-CH3
-COOH
-OCH2CF3
-OH
-COOCH3
-OC6H5
-NH2
-NHCOCH3
-EG3-OH
Probability
SSD (Å)


TGTG-D-GTGT peptide
-CH3
-COOH
-OCH2CF3
-OH
-COOCH3
-OC6H5
-NH2
-NHCOCH3
-EG3-OH
Probability
SSD (Å)


TGTG-F-GTGT peptide
Probability
SSD (Å)
-CH3
-COOH
-OCH2CF3
-OH
-COOCH3
-OC6H5
-NH2
-NHCOCH3
-EG3-OH

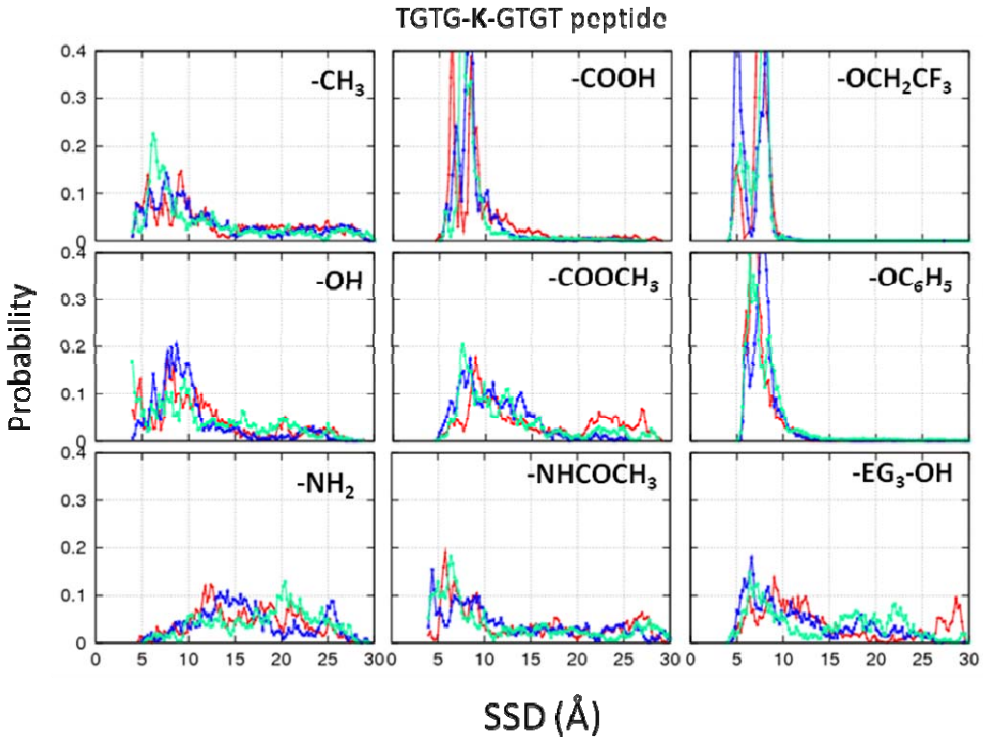
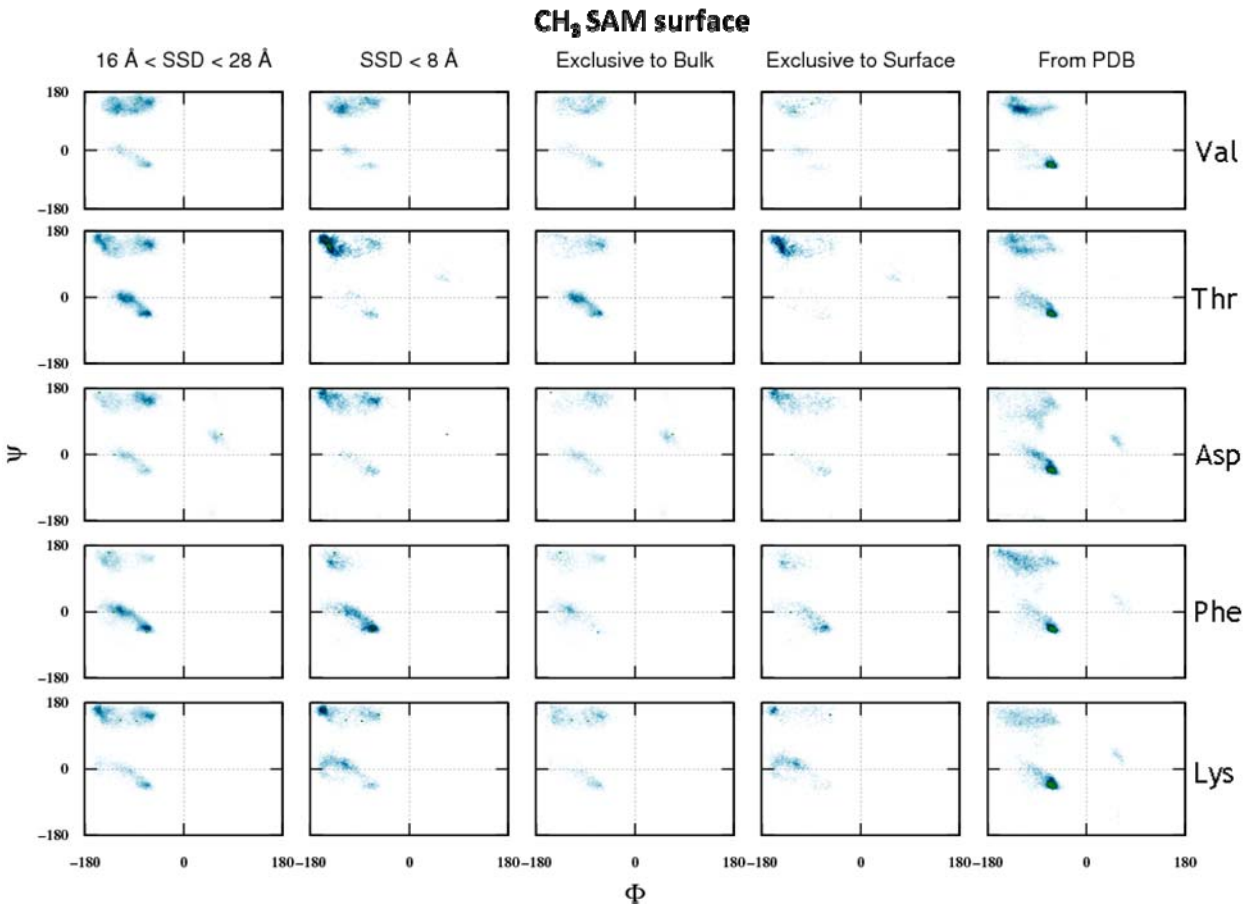
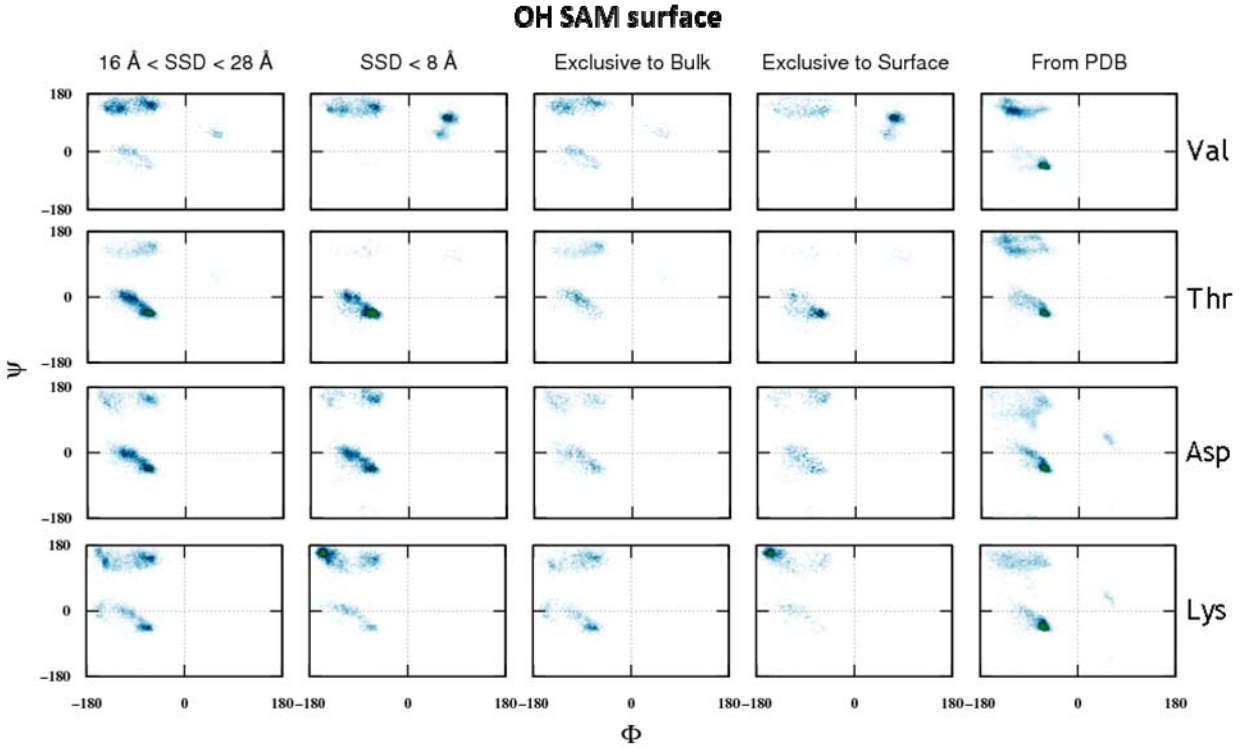
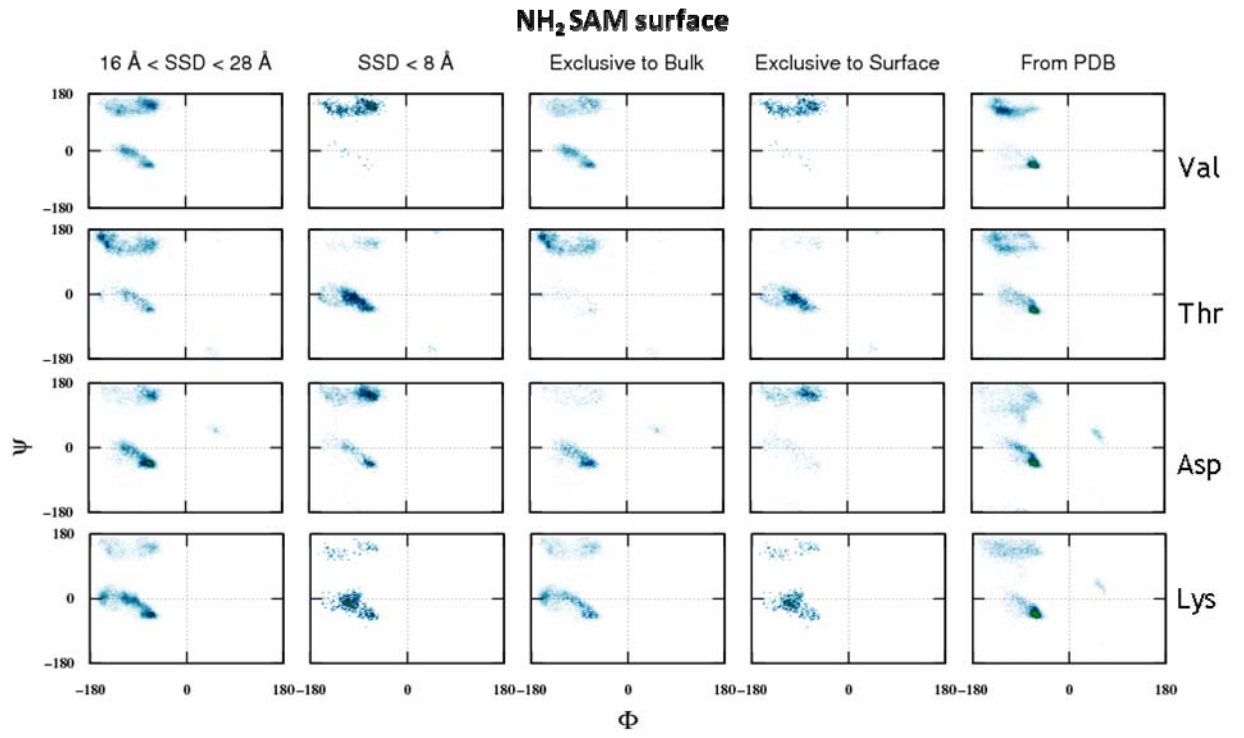

TGTG-K-GTGT peptide
Probability
SSD (Å)
-CH3
-COOH
-OCH2CF3
-OH
-COOCH3
-OC6H5
-NH2
-NHCOCH3
-EG3-OH

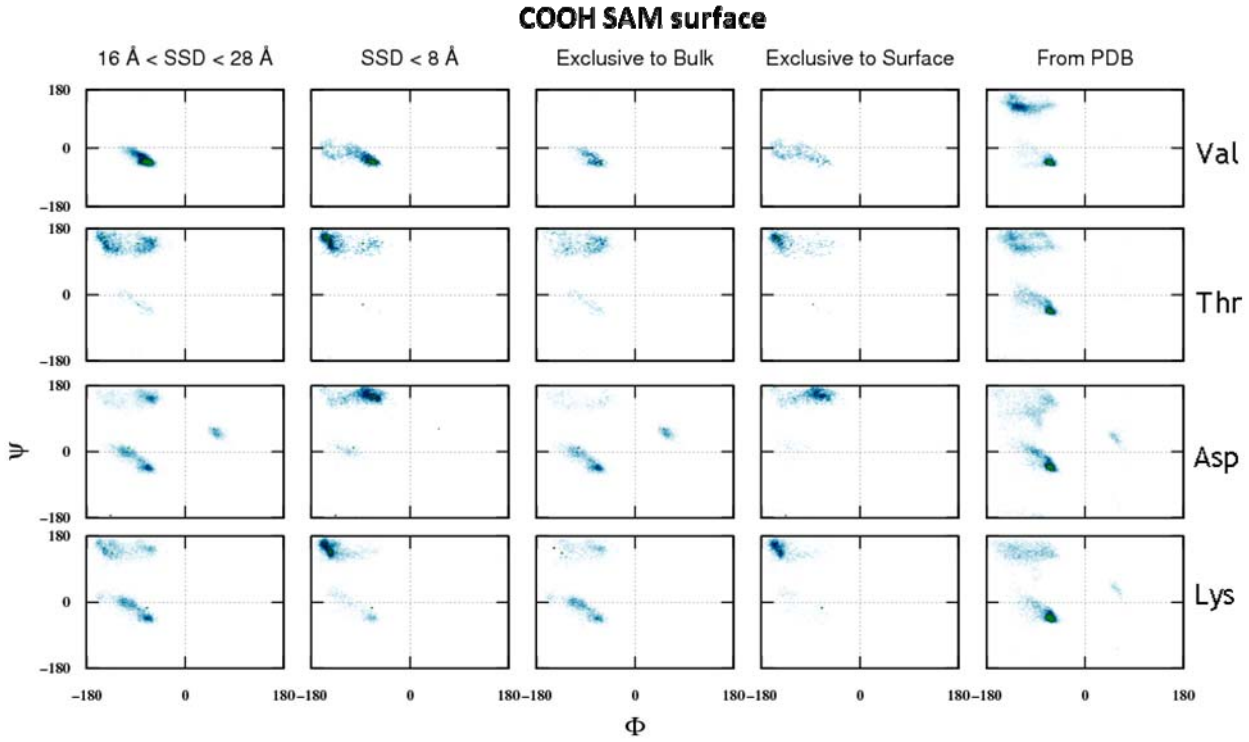
Figure S.3: Ramachandran plots for the dihedral angles of the midchain guest residue (X) from the biased-REMD simulations for each of the TGTG-X-GTGT peptides on different SAM surfaces. The first column in each plot shows the ϕ/ψ dihedral angle distribution for the guest residue (Val (V), Thr (T), Asp (D), Phe (F), or Lys (K)) when the peptide's SSD is between 16 – 28 Å, representing bulk conditions. The second column shows the dihedral angle distribution of the peptide's guest residue when the center of mass of peptide is very close to the surface (SSD < 8 Å). The third and fourth columns illustrate differences between the bulk and adsorbed structures (obtained by subtracting bin counts of the solution plots from the bin counts of the surface plots), with the third column indicating conformations formed in solution but not on the surface and the fourth column indicating conformations formed on the surface but not in bulk solution. The fifth column displays the dihedral distribution for Val, Thr, Asp, Phe, and Lys exhibited by 500 representative PDB protein crystal structures.[1] Most of the peptides exhibit close agreement between the amino acid conformations obtained from the biased-REMD simulations in bulk condition and the conformations from the PDB crystal structures providing evidence that adequate conformational sampling was obtained for each of the TGTG-X-GTGT peptides in the biased-REMD simulations.

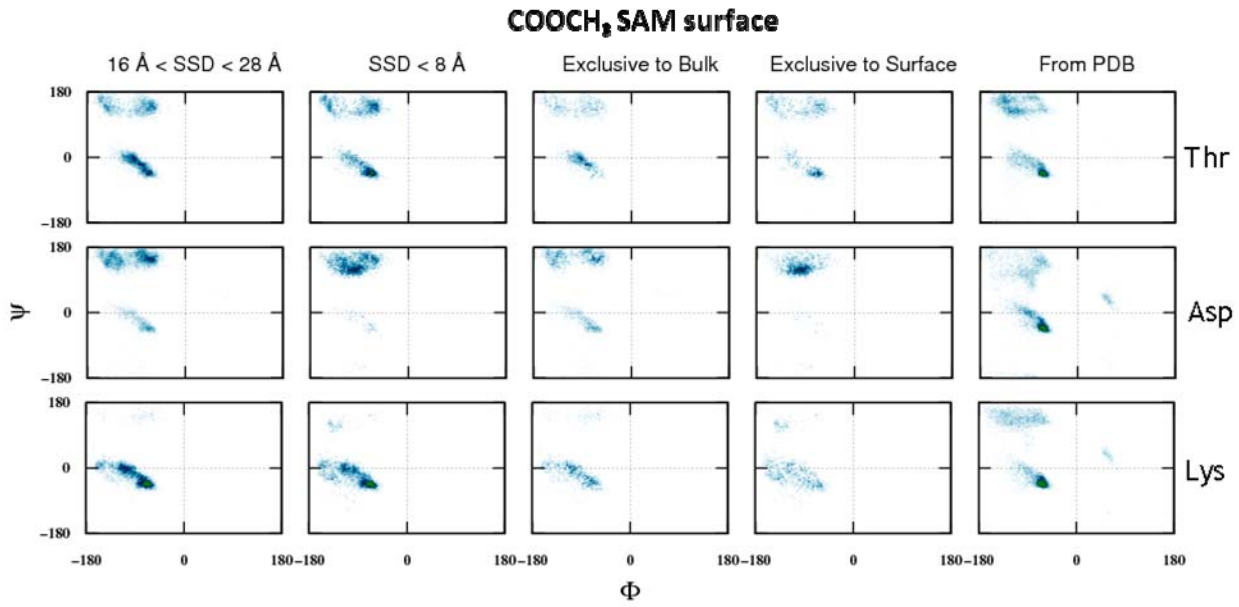
1. Lovell, S. C.; Davis, I. W.; Adrendall, W. B.; de Bakker, P. I. W.; Word, J. M.; Prisant, M. G.; Richardson, J. S.; Richardson, D. C., *Proteins-Structure Function and Genetics* **2003,** *50* (3), 437-450.

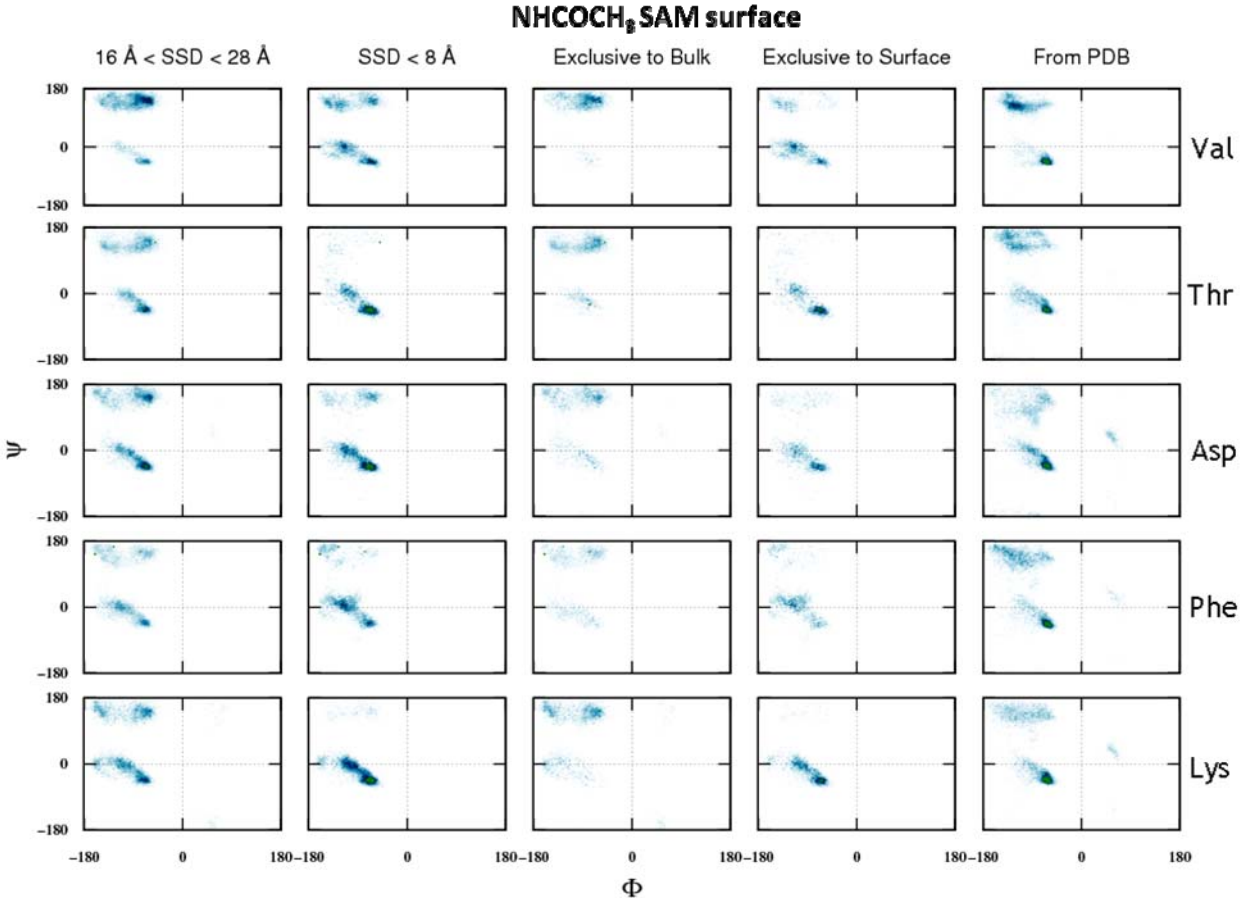

CH3 SAM surface
16 Å < SSD < 28 Å
SSD < 8 Å
Exclusive to Bulk
Exclusive to Surface
From PDB
Val
Thr
Asp
Phe
Lys
ψ
Φ
180
0
−180

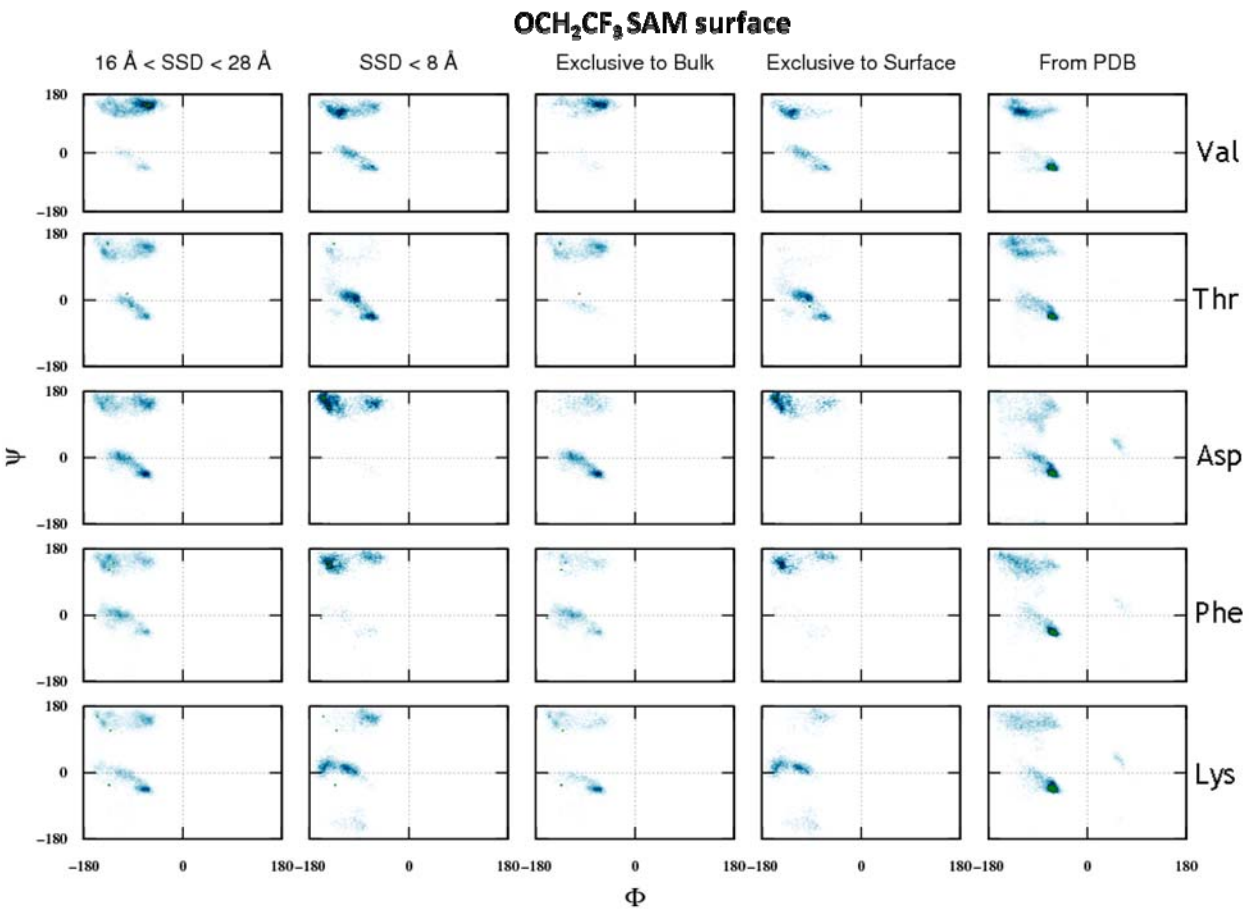

OH SAM surface
16 Å < SSD < 28 Å
SSD < 8 Å
Exclusive to Bulk
Exclusive to Surface
From PDB
Val
Thr
Asp
Lys
ψ
Φ
180
0
−180

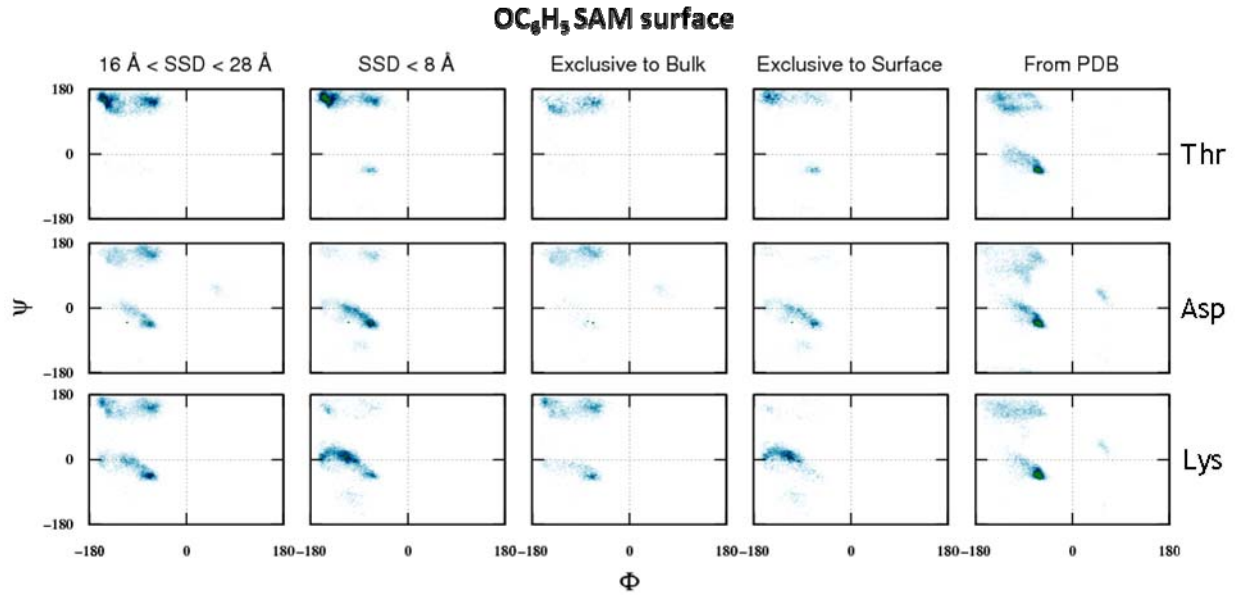

NH2 SAM surface
16 Å < SSD < 28 Å
SSD < 8 Å
Exclusive to Bulk
Exclusive to Surface
From PDB
Val
Thr
Asp
Lys
ψ
Φ
180
0
−180

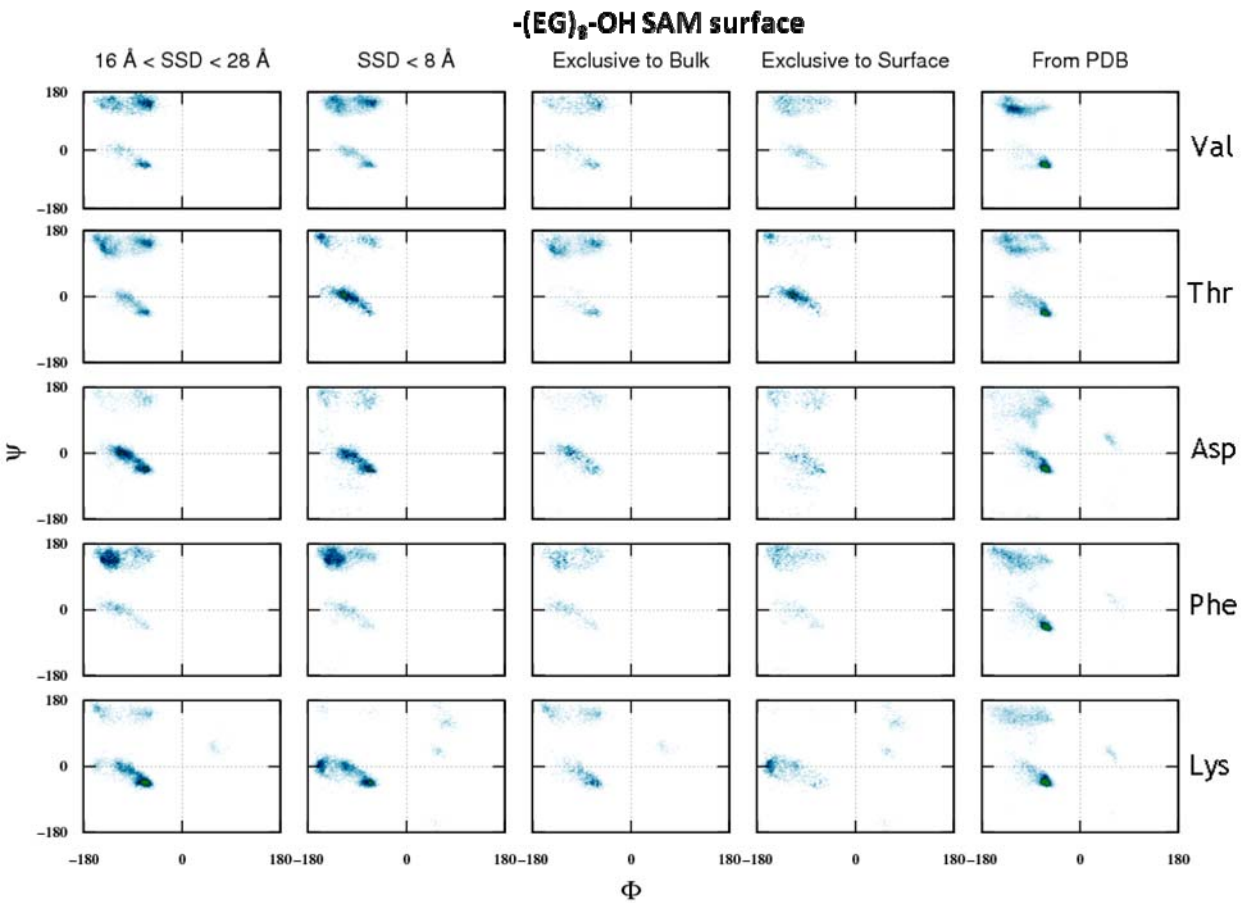

COOH SAM surface
16 Å < SSD < 28 Å
SSD < 8 Å
Exclusive to Bulk
Exclusive to Surface
From PDB
Val
Thr
Asp
Lys
ψ
Φ
180
0
−180


COOCH3 SAM surface
16 Å < SSD < 28 Å
SSD < 8 Å
Exclusive to Bulk
Exclusive to Surface
From PDB
Thr
Asp
Lys
ψ
Φ
180
0
−180


NHCOCH3 SAM surface
16 Å < SSD < 28 Å
SSD < 8 Å
Exclusive to Bulk
Exclusive to Surface
From PDB
Val
Thr
Asp
Phe
Lys
ψ
Φ
180
0
−180


OCH2CF3 SAM surface
16 Å < SSD < 28 Å
SSD < 8 Å
Exclusive to Bulk
Exclusive to Surface
From PDB
Val
Thr
Asp
Phe
Lys
ψ
Φ
180
0
−180


OC6H5 SAM surface
16 Å < SSD < 28 Å
SSD < 8 Å
Exclusive to Bulk
Exclusive to Surface
From PDB
Thr
Asp
Lys
ψ
Φ
180
0
−180


-(EG)8-OH SAM surface
16 Å < SSD < 28 Å
SSD < 8 Å
Exclusive to Bulk
Exclusive to Surface
From PDB
Val
Thr
Asp
Phe
Lys
ψ
Φ
180
0
−180