Supporting Information for: Elucidating Polymorph-selective Bio-adsorption on Chitin Surfaces

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Umbrella	Distance (nm)
1	3.50
2	3.25
3	3.00
4	2.75
5	2.50
6	2.25
7	2.00
8	1.80
9	1.70
10	1.60
11	1.50
12	1.40
13	1.30

Table S1: Centre of mass distances used for the harmonic potential applied to each umbrella.

	Ala		Asp		Asn		Tyr	
Umbrella	centre	$k1$	centre	$k1$	centre	$k1$	centre	$k1$
1	-0.465	500	-0.793	500	-0.500	500	-0.540	500
2	-0.380	500	-0.653	500	-0.391	500	-0.407	500
3	-0.272	500	-0.495	500	-0.300	500	-0.275	500
4	-0.143	500	-0.284	500	-0.172	500	-0.262	500
5	-0.063	1000	-0.266	1000	-0.99	500	-0.192	500
6	0.124	500	0.103	500	0.078	500	0.072	1000
7			0.190	500	0.204	500		

Table S2: Harmonic restraints locations and force constants used for the amino acid inclusion umbrella sampling simulations.

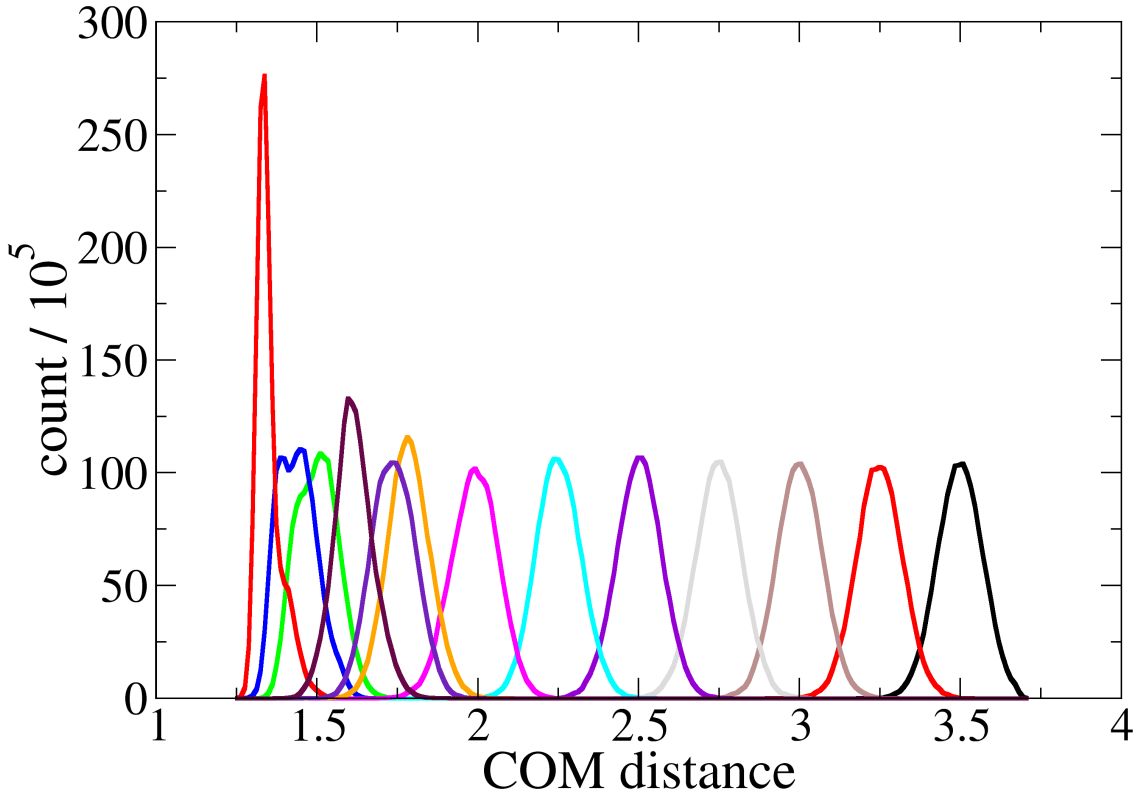

Figure S1: Exemplar umbrella histogram, produced from the umbrella simulations of Ala at the aqueous α-chitin [100] interface.

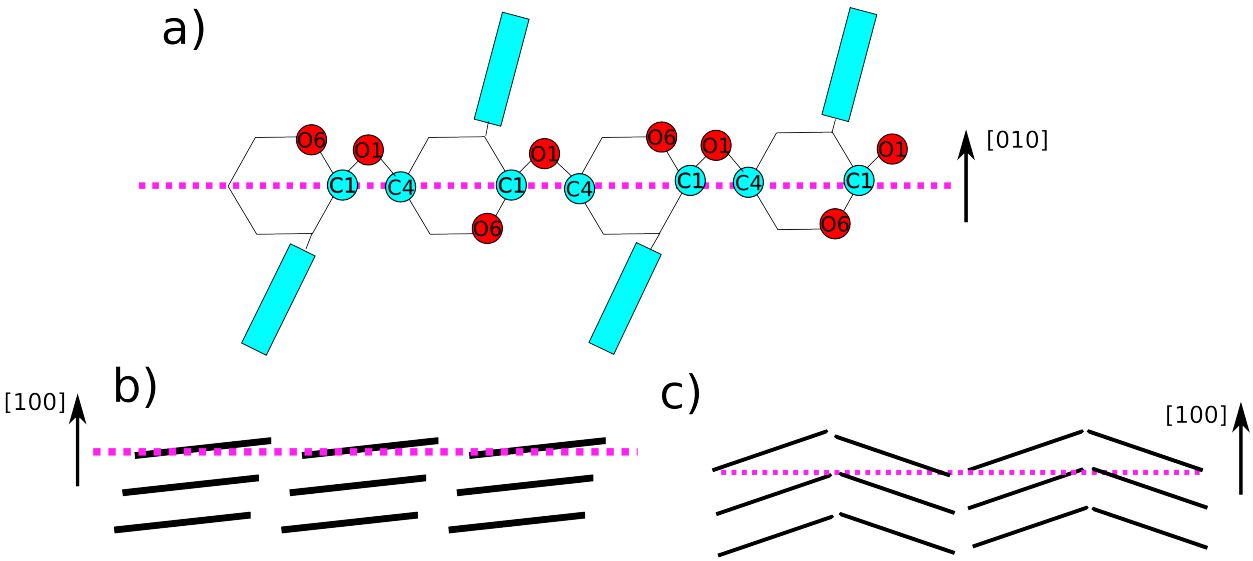

Figure S2: Baseline used to denote the top of each chitin interface for a) the aqueous [010] interfaces, b) the β[100] interface and c) the α[100] interface.

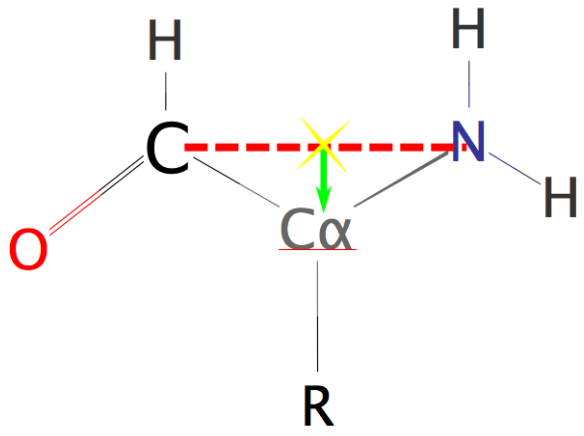

Figure S3: Schematic of the vector used to determine the orientation of the amino acids at each interface.

Residue	Site
Ala	C_β
Asp	C_γ
Glu	C_δ
Lys	N_Z
Arg	C_Z
Asn	N_δ
Cys	SZ
Tyr	Geometric Centre of Ring
Trp	Geometric Centre of Ring

Table S3: Sites used for the calculation of distance between the interaction site on each amino acid and the chitin surface.

Amino Acid	$\alpha[100]$	$\beta[100]$	$\alpha[010]$	$\beta[010]$
Ala	-0.82 ± 0.67	-1.61 ± 0.63	-6.27 ± 0.96	-1.06 ± 1.34
Arg	-0.49 ± 0.92	$\mathbf{-4.49 \pm 0.64}$	-9.25 ± 1.31	-0.01 ± 2.41
Asn	-2.03 ± 0.63	-0.28 ± 0.56	-5.39 ± 1.13	-8.51 ± 1.48
Asp	-1.30 ± 0.71	-0.91 ± 0.66	-1.93 ± 1.50	-0.60 ± 1.06
Cys	0.01 ± 0.59	-2.99 ± 0.82	-5.30 ± 0.83	-3.36 ± 1.40
Glu	-1.11 ± 0.82	-1.42 ± 0.55	-2.16 ± 1.37	1.13 ± 1.73
Lys	0.48 ± 0.66	-0.67 ± 0.81	-5.26 ± 1.09	-1.74 ± 1.33
Trp	$\mathbf{-2.31 \pm 0.69}$	-3.56 ± 0.87	$\mathbf{-9.44 \pm 1.40}$	$\mathbf{-9.00 \pm 2.32}$
Tyr	-0.91 ± 0.72	-4.07 ± 0.54	-6.45 ± 2.60	-3.57 ± 2.03

Table S4: Binding free energy values ($kJmol^{-1}$) for the nine representative amino acids, for all four aqueous chitin interfaces. The most strongly adsorbing amino acid to each surface is indicated in bold.

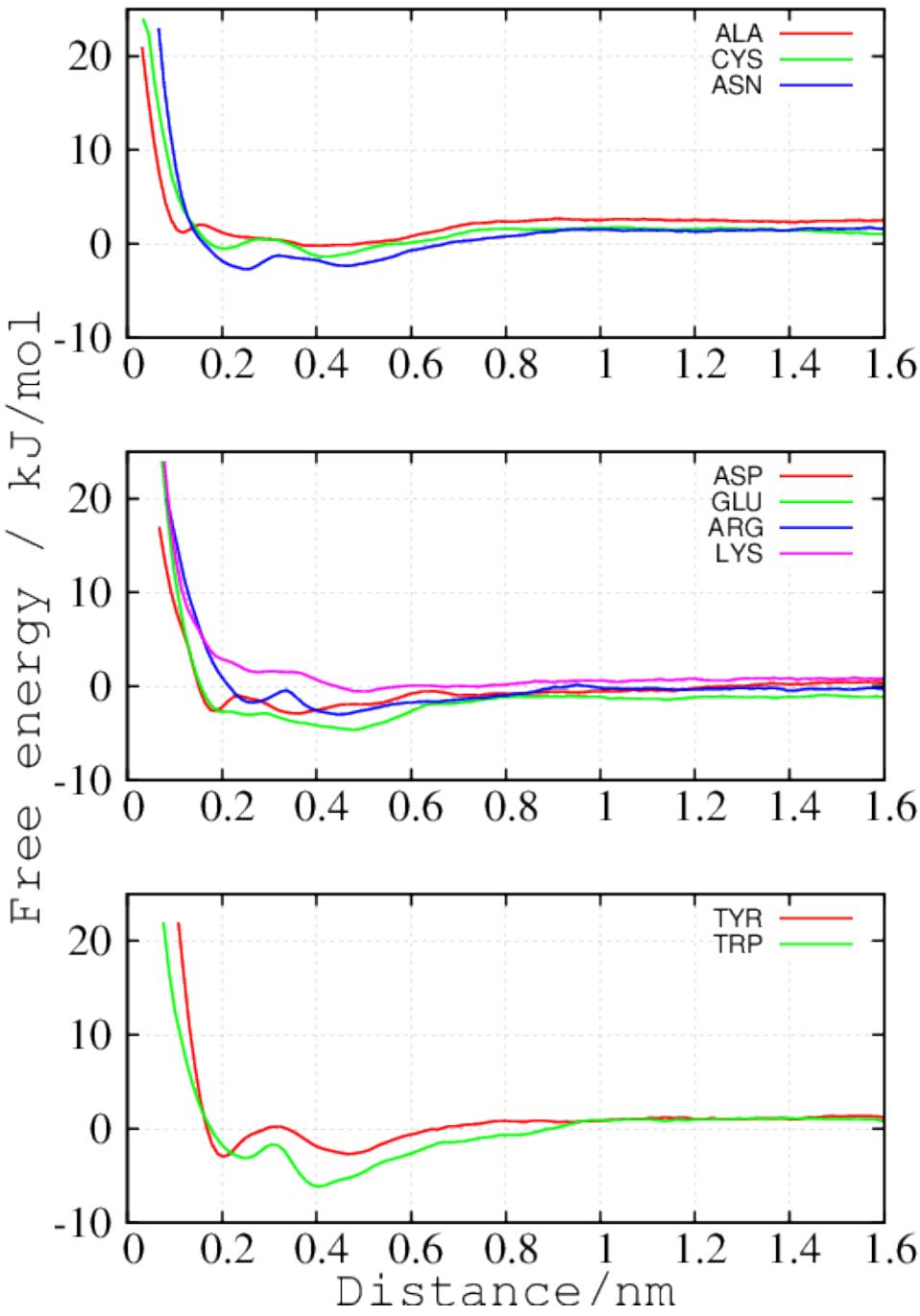

Figure S4: Adsorption free energy profiles for nine representative amino acids at the aqueous $\alpha[100]$ interface.

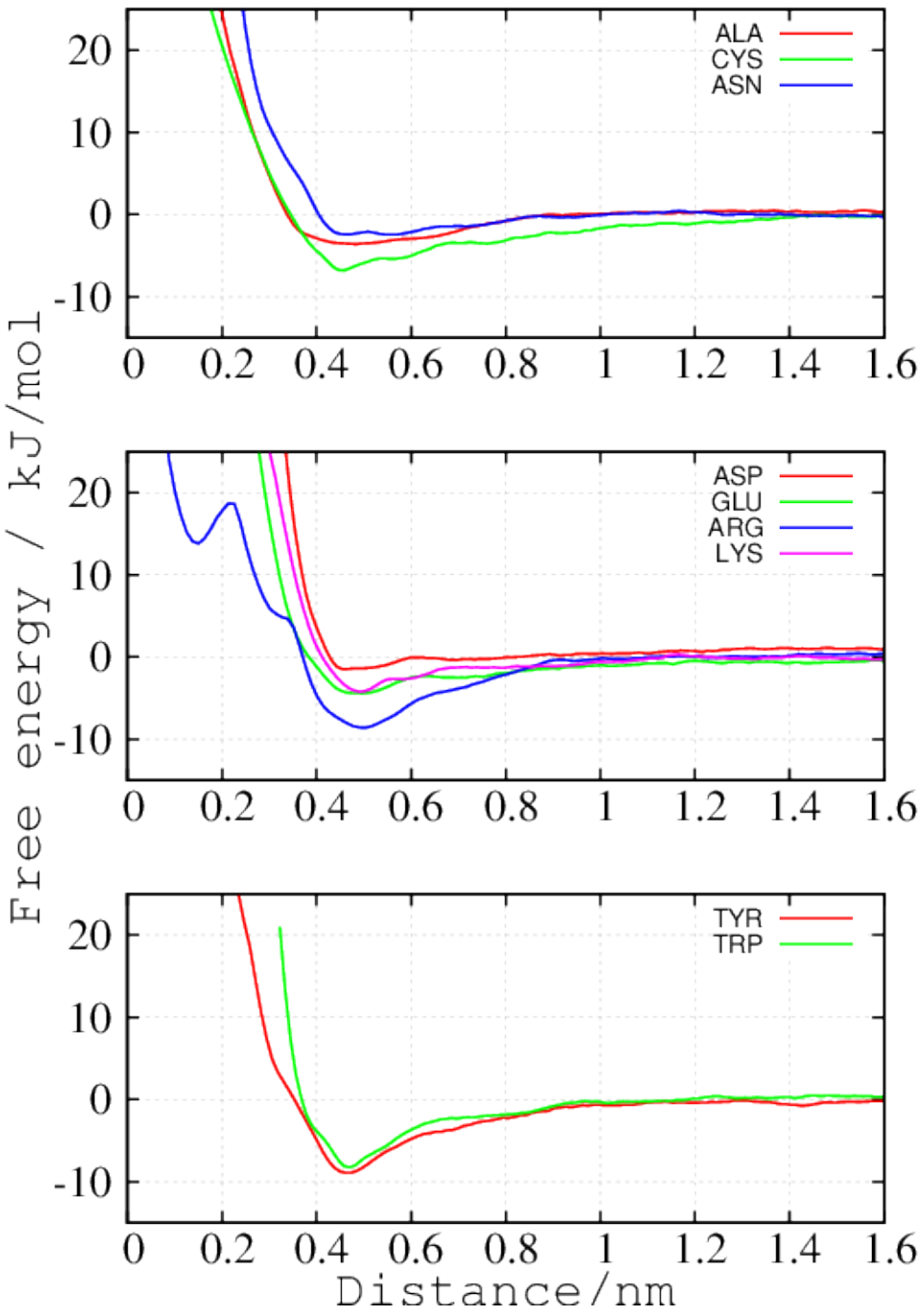

Figure S5: Adsorption free energy profiles for nine representative amino acids at the aqueous $\beta[100]$ interface.

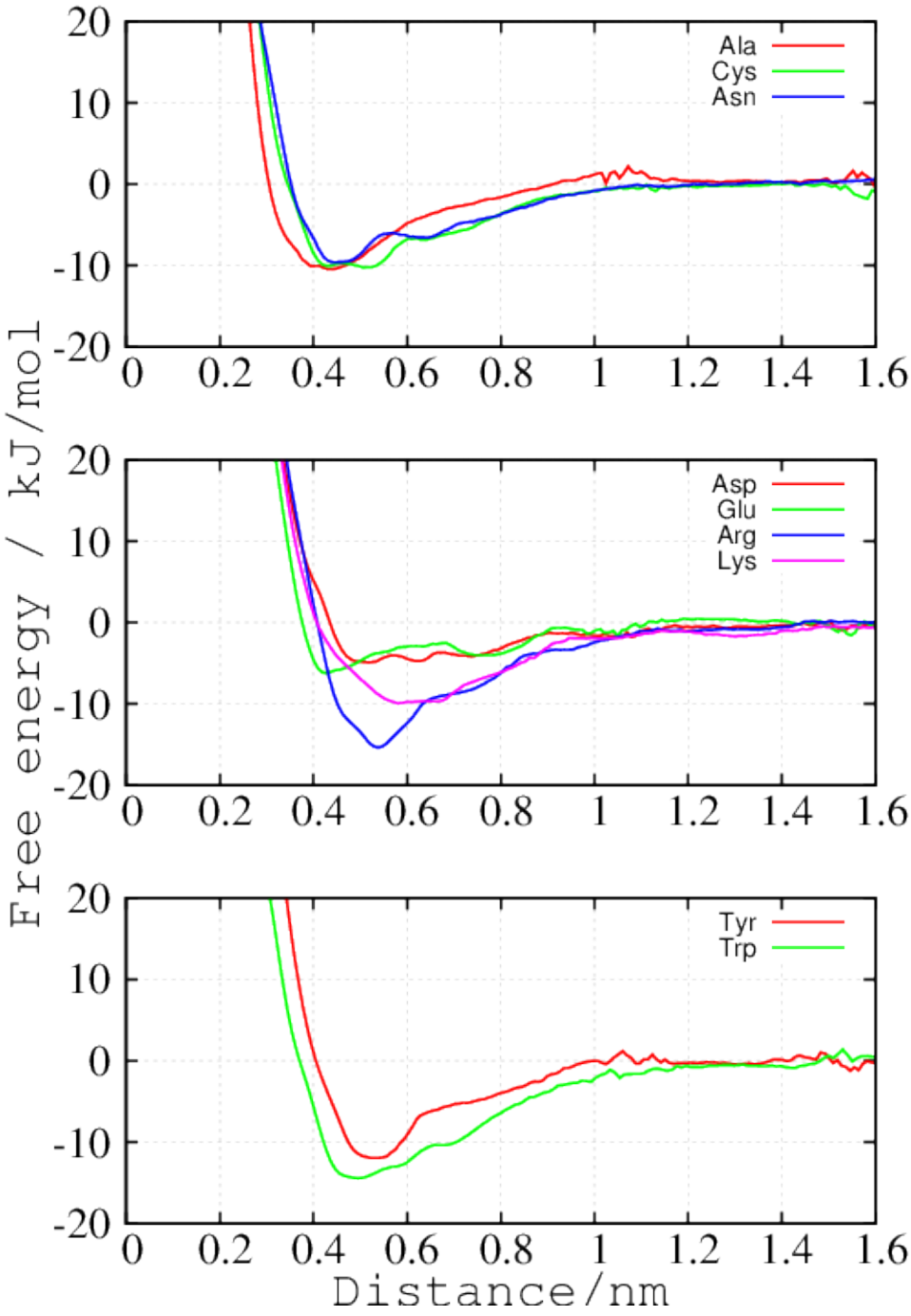

Figure S6: Adsorption free energy profiles for nine representative amino acids at the aqueous $\alpha[010]$ interface.

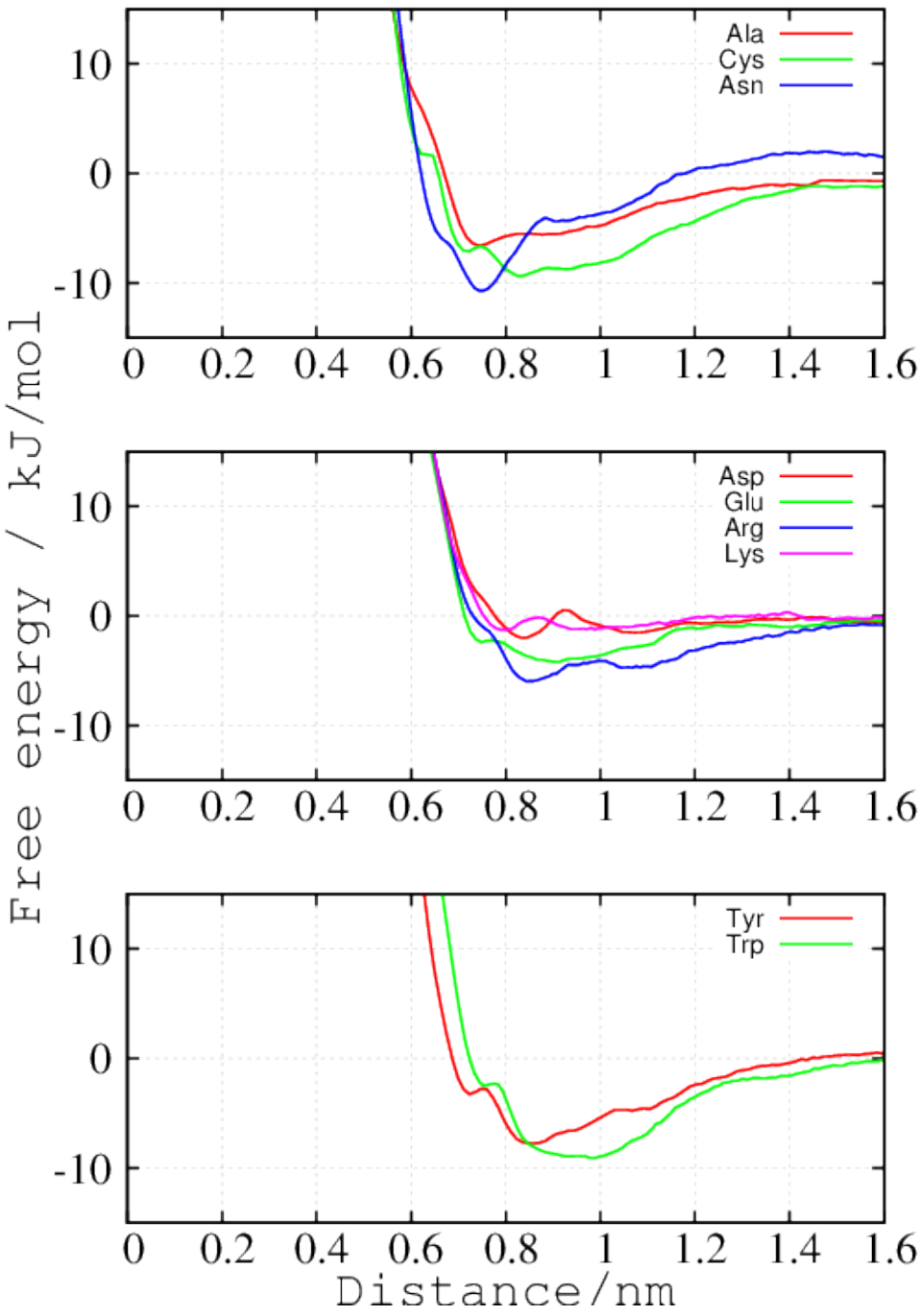

Figure S7: Adsorption free energy profiles for nine representative amino acids at the aqueous $\beta[010]$ interface.

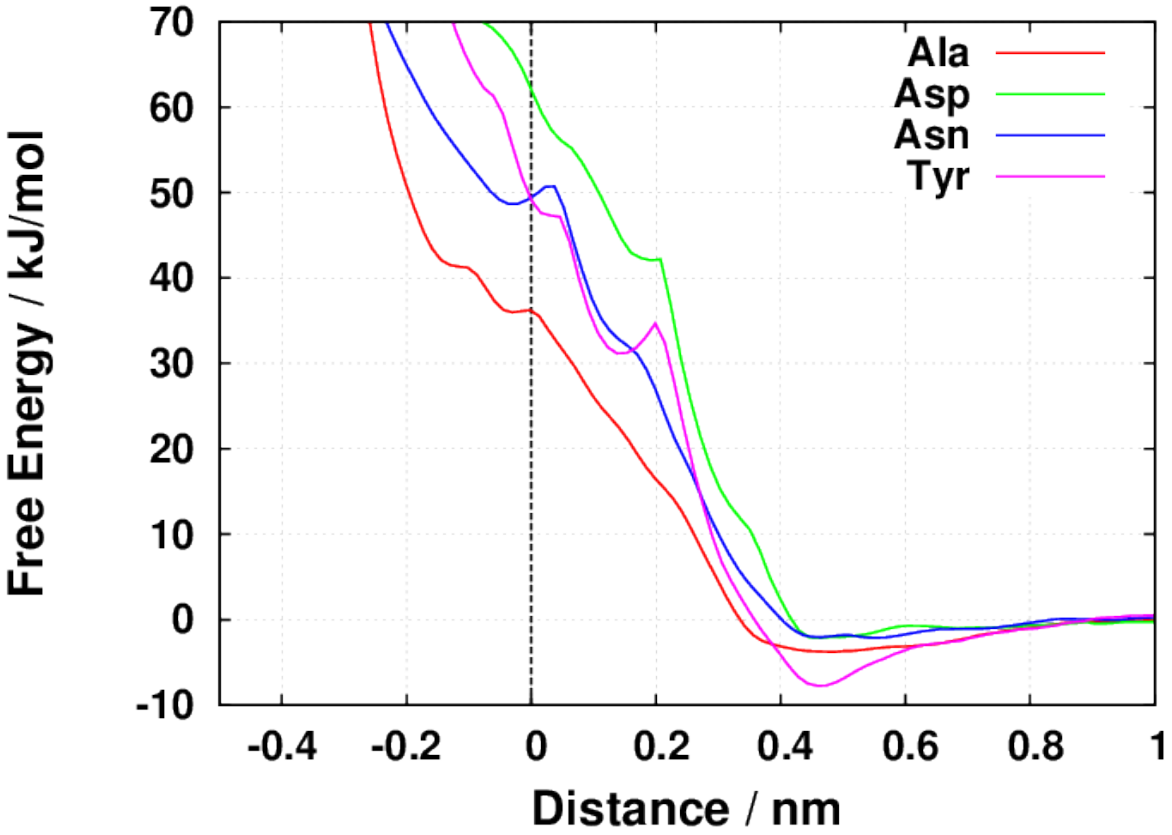

Figure S8: Free energy profiles for the inclusion of four amino acids into the β-chitin crystal from the aqueous [100] interface.