Electronic Supplementary Material (ESI) for Chemical Science
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SUPPORTING INFORMATION

TABLE S1. MD simulation details. The most energetically favourable orientation for each surface is shown in bold and underlined. All simulations were performed for 100 ns.

MPMN Surface Composition	Sim. Cell Dimensions (nm)	Ligand No. and Widths (nm)	No. of Water Molecules	No. of Ions
"Control" surfaces				
1:1 OT:MH 'Janus'	6.0 x 6.3 x 8.5	OT:168, 3.15 MH: 168, 3.15	o1[+]:8161 o2:8157 o3:8108	20 Na^+ 28 Cl^-
1:1 OT:MH 'random'	6.0 x 6.3 x 8.5	OT:168, N/A MH:168, N/A	o1:8126 o2:8122 o3:8072	20 Na^+ 28 Cl^-
1:1 OT:MH 'thin, tilted'	6.0 x 6.0 x 8.5	OT:150, 0.6 MH:150, 0.6	o1:8027 o2:8034 o3:7982	20 Na^+ 28 Cl^-
MPMN surfaces				
Pure OT	6.0 x 6.3 x 8.5	OT:336, N/A	o1:8310 o2:8305 o3:8258	20 Na^+ 28 Cl^-
2:1 OT:MH	6.0 x 7.2 x 8.5	OT:256, 1.2 MH:128, 0.6	o1:9616 o2:9609 o3:9568	23 Na+ 31 Cl-
1:1 OT:MH 'thin'	6.0 x 6.0 x 8.5	OT:192, 0.6 MH:192, 0.6	o1:7940 o2:7946 o3:7903	20 Na+ 28 Cl-
1:1 OT:MH 'thick'	6.0 x 7.2 x 8.5	OT:160, 0.9 MH:160, 0.9	o1:9666 o2:9669 o3:9632	23 Na+ 31 Cl-
1:2 OT:MH	6.0 x 7.2 x 8.5	OT:128, 0.6 MH:256, 1.2	o1:9702 o2:9705 o3:9662	23 Na+ 31 Cl-
Pure MH	6.0 x 6.3 x 7.4	MH:336, N/A	o1:7190 o2:7153 o3:8522	17 Na+ 25 Cl-

[+] o1, o2 and o3 refer to the 3 different Lyz initial orientations studied for each MPMN surface

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FIGURE S1. Binding energies averaged over the final 20 ns of each simulation, given as a sum of the binding enthalpy (black bars) and desolvation energy (white bars). Asterisks (*) indicate most energetically favourable Lyz binding orientation for each surface. Orientations marked with "X" indicate that Lyz desorbed and was not in contact with the surface over the final 20 ns of simulation.

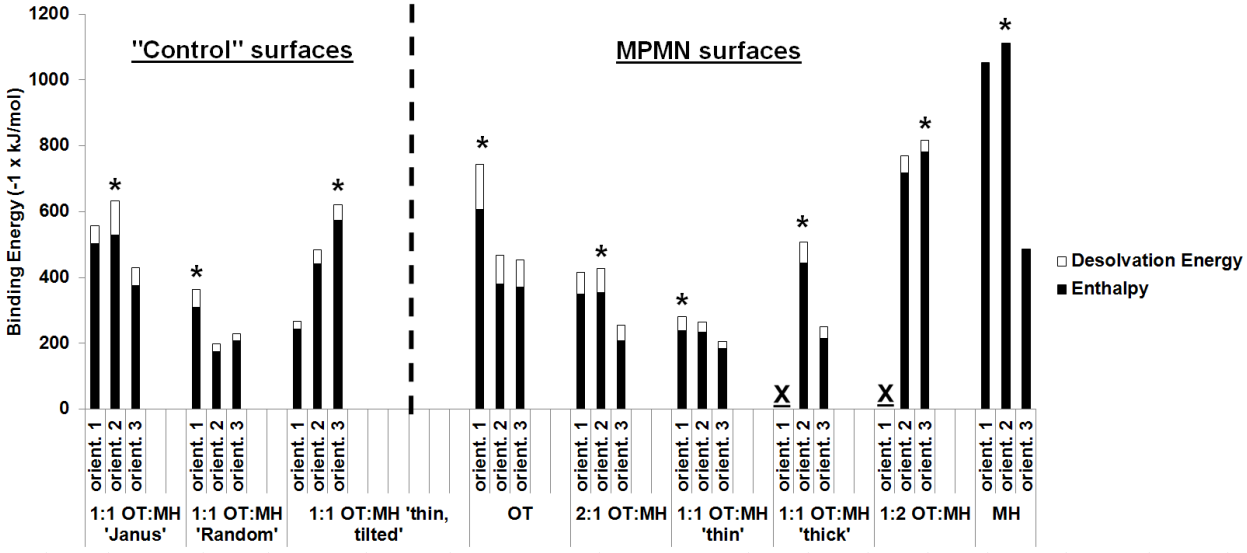

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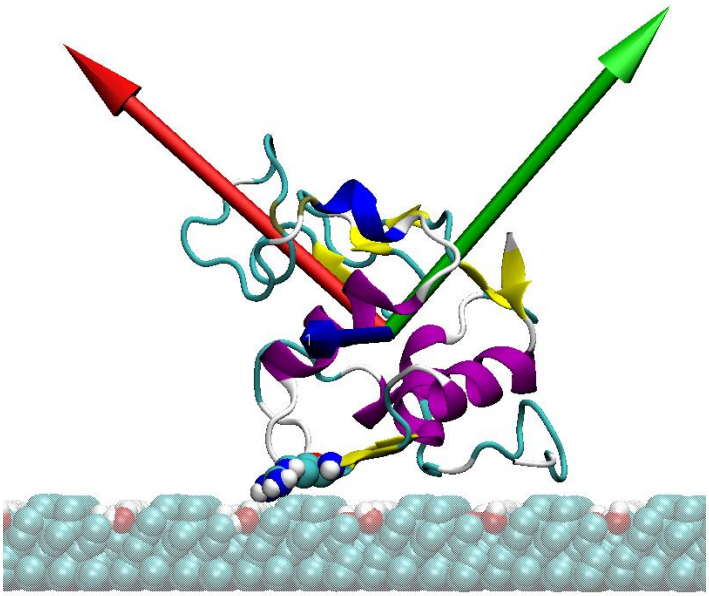
FIGURE S2. A) Most energetically favourable Lyz binding orientations on the 1:1 OT:MH 'thin, tilted' surface. Lyz backbone represented as ribbons and colour-coded by secondary structure (purple=α-helix, yellow=β-strand, blue=π-helix, cyan=turn). Principal axes vectors are shown to illustrate orientation, with PA1 (longest axis)=red, PA2=green and PA3 (shortest)=blue. **B)** Average number of contacts with OT (black bars) and MH (white bars) for each Lyz residue at the 1:1 OT:MH 'thin, tilted' surface. Atoms of a given residue are considered to be in contact with a ligand if they fall within 4.5 Å of any OT/MH atom.

A)



B)

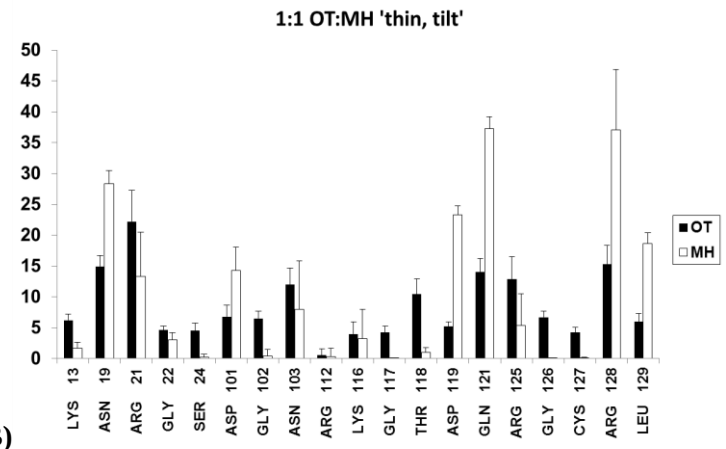


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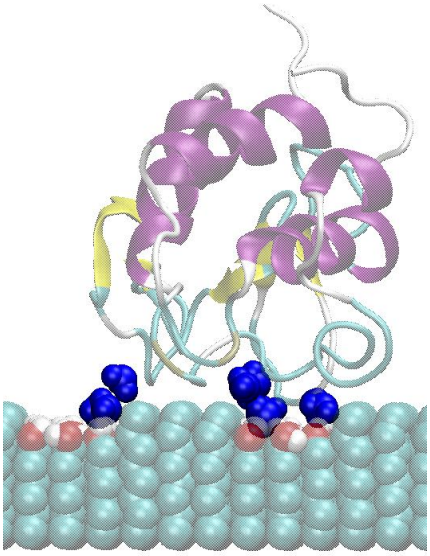
FIGURE S3. A) Illustration of interfacial waters trapped between Lyz and the 1:1 'thick' surface. Waters are shown as blue spheres. **B-F)** Average number of contacts for each residue with "sandwiched" waters for **B)** 2:1; **C)** 1:1 'thin'; **D)** 1:1 'thick'; **E)** 1:2 OT:MH surfaces; **F)** pure MH; and **G)** 1:1 'random' surfaces. Residues which make contacts with sandwiched waters but *not* directly with the MPMN ligands are marked with asterisks.

A)



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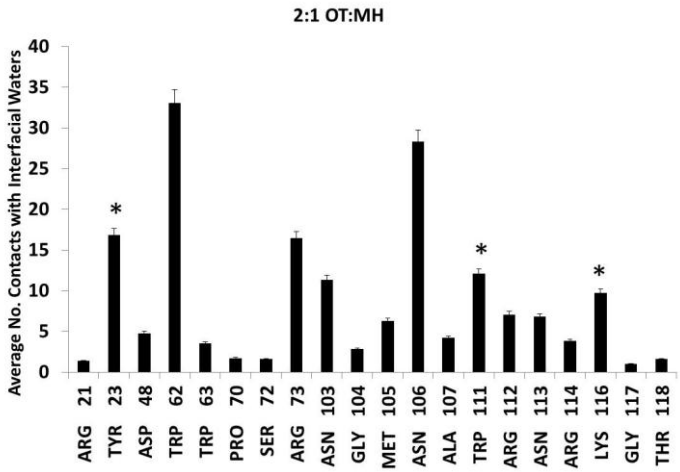

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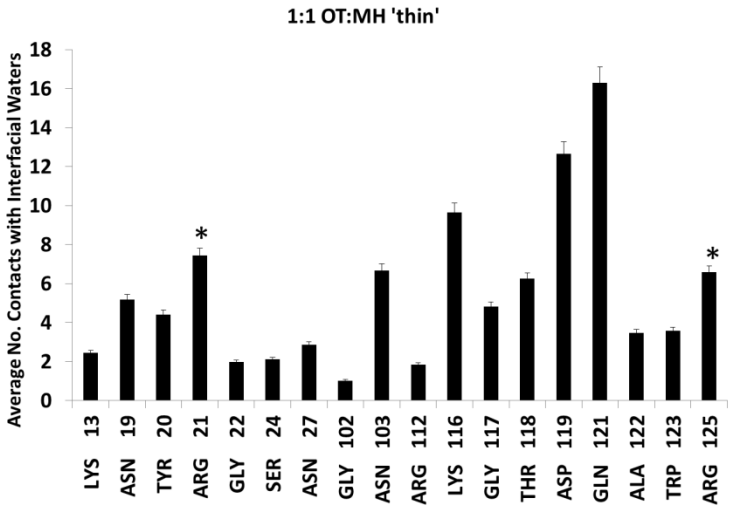
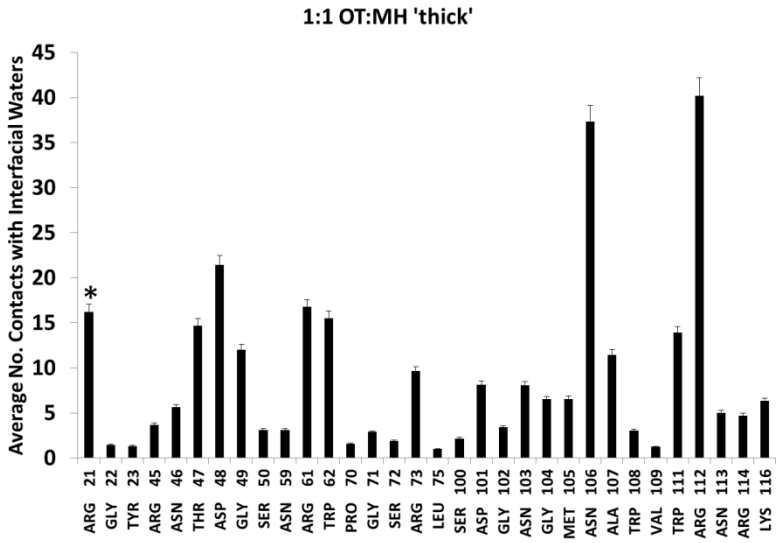
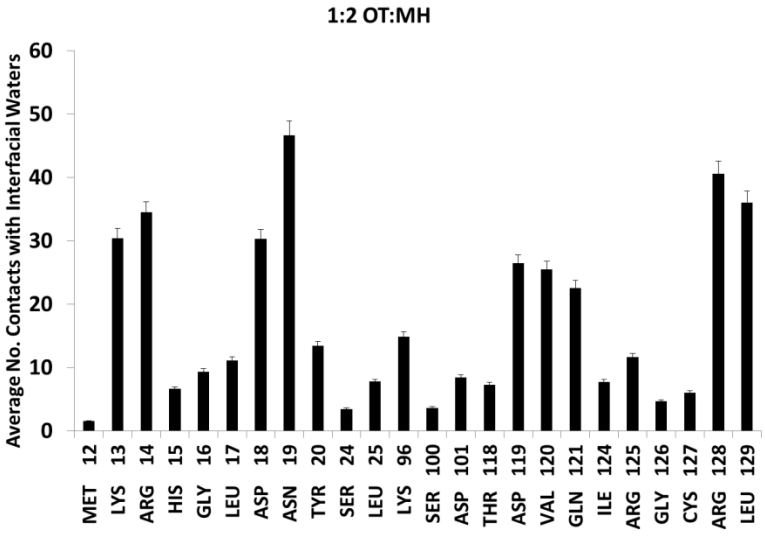
C)



D)



E)



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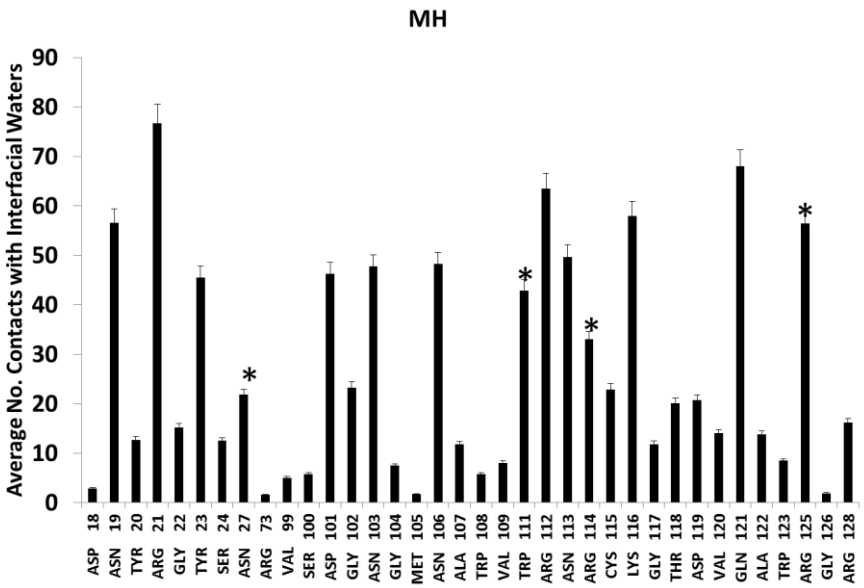
F)



G)

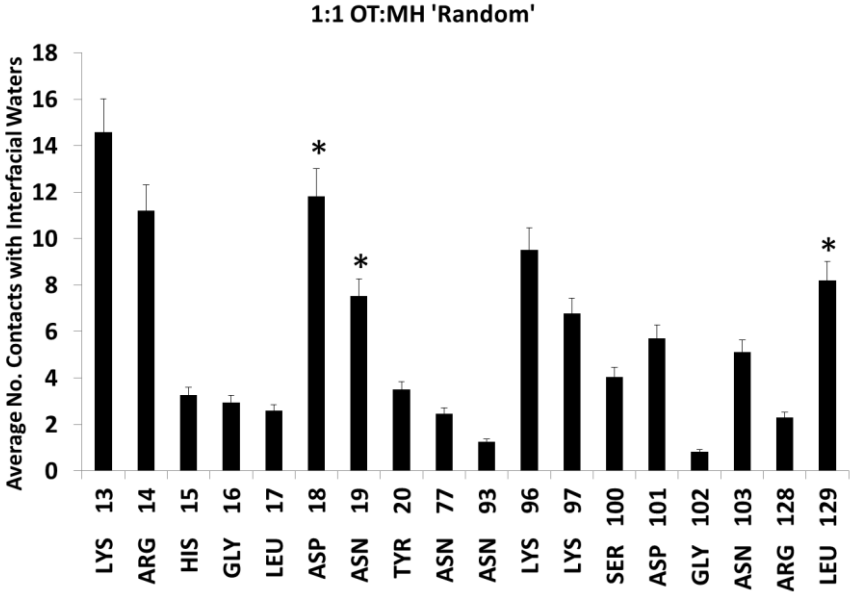


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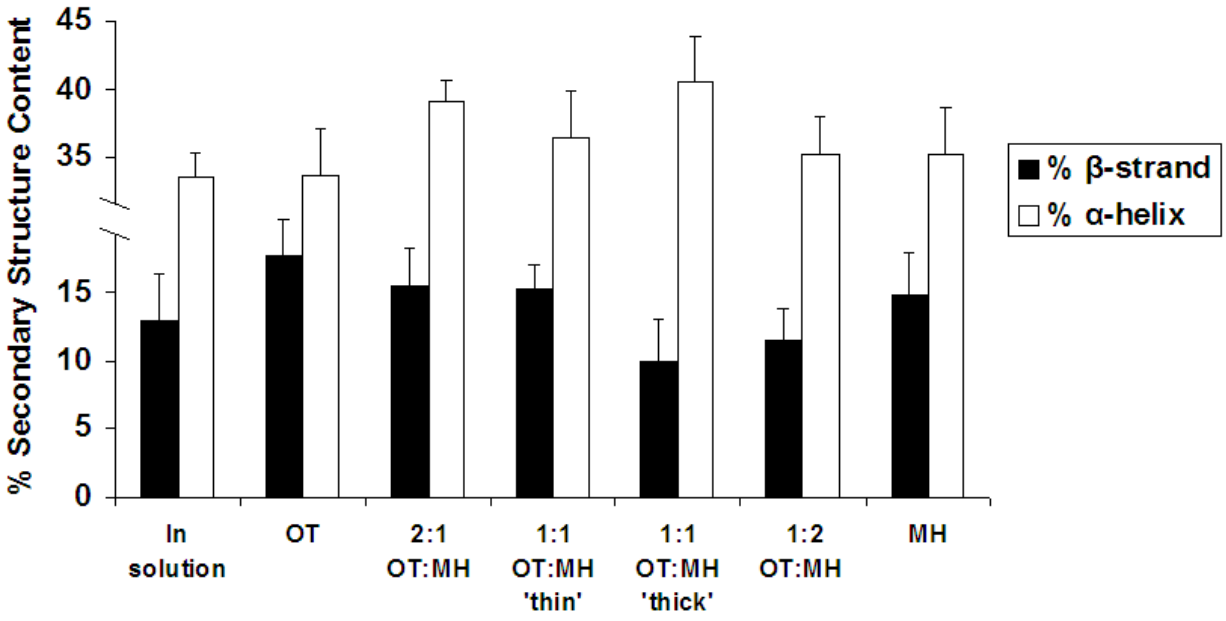
FIGURE S4. Percentage (%) of the lysozyme chain that exhibits secondary structural content (black=β-strand, white=α-helix), averaged over the final 20 ns of simulations with respect to MPMN composition. For each composition, data is shown only for the orientation with the *highest* surface interaction enthalpy.



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Effects of ligand tilt for the 1:1 OT:MH 'thin' surface

In order to examine some of the influences of ligand tilt on Lyz adsorption to a nanopatterned surface, we have simulated adsorption of Lyz on a tilted version of the 1:1 OT:MH 'thin' surface, in which the surface ligands exhibit approximately 30^{o} tilt with respect to the surface normal (Fig. S2A). Three initial orientations were simulated using the same computational protocol described in Methods (see main manuscript). We have characterised the binding energy (enthalpy and desolvation energy), binding orientation and surface contact residues of Lyz adsorption to the tilted surface and compared the results to those of the "untilted" 1:1 surface.

We find that the predicted binding energies are higher than those predicted for the untilted 1:1 surface (Fig. S1), and suggests that there are higher numbers of Lyz-surface contacts at the tilted surface. This may be owing to the greater exposure of surface hydroxyl groups as a result of the tilt. Examination of the residue contact profile of the tilted surface (Fig. S2B) confirms that there is indeed a greater number of Lyz residues in contact with the MH ligands, as well as great number of contacts per residue. However, there are also similarities in the adsorption characteristics for both tilted and untilted surfaces. The overall orientation of adsorbed Lyz is similar on both surfaces, with the first principal axis lying at approximately 45^{o} with respect to the surface normal in both cases (cf. Fig. 2 with Fig. S2A). More importantly, Lyz adsorbs to both surfaces at the same face, as can be ascertained by inspection of the main contact residues in Fig. 4C and S2B (for example, Asn103 and Gln101 are important contacts at both surfaces). Thus, our simulation results suggest that while the association between Lyz and a tilted nanopatterned surface may be greater than an untilted counterpart, the binding orientation, contact residues and (therefore) post-adsorption catalytic activity of Lyz is predicted to be similar regardless of ligand tilt.