

Supporting Information

Enhancement of electronic effects at a Biomolecule- Inorganic Interface by Multivalent Interactions

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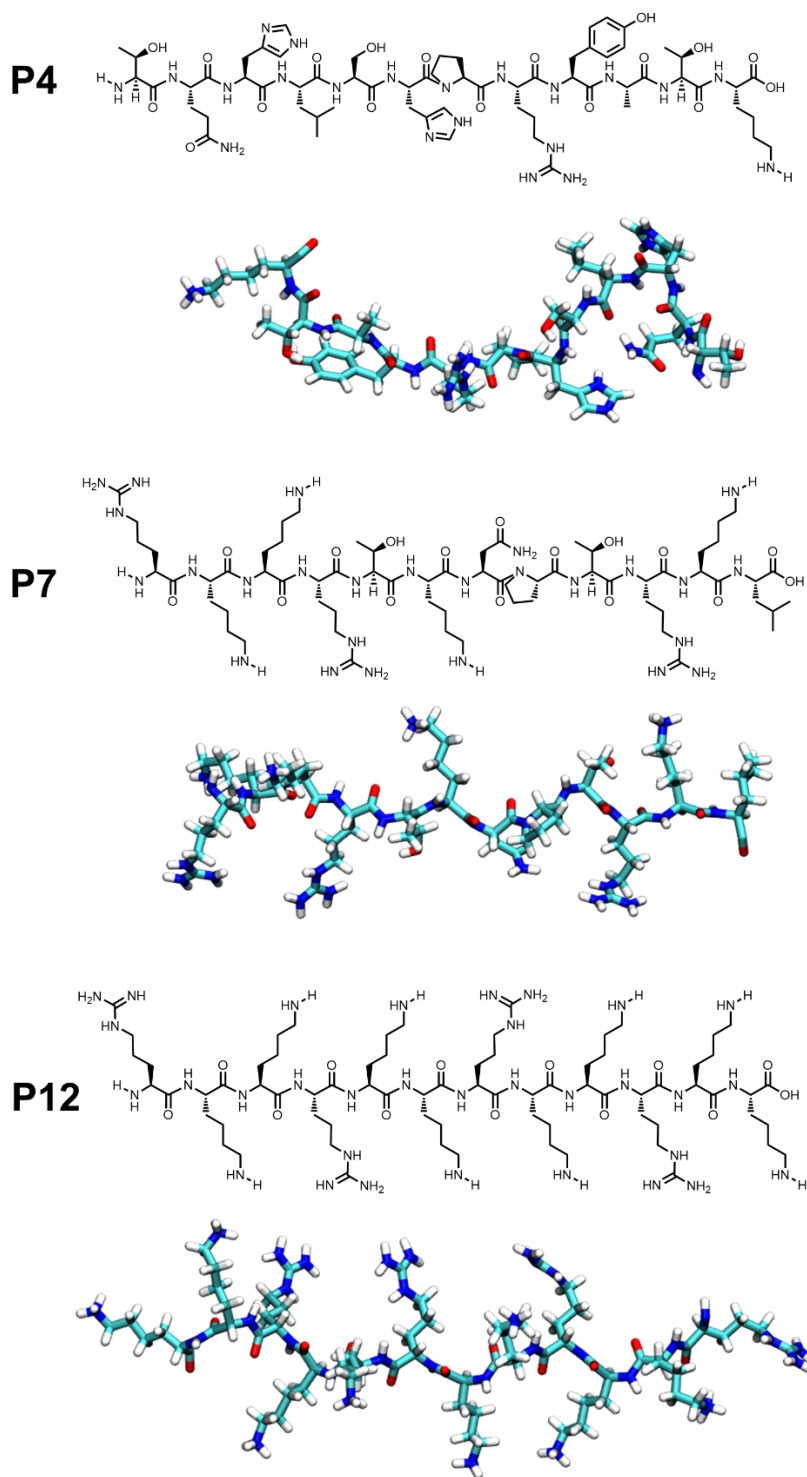


Figure S1. Chemical structure and representative model structure in solution of the peptide molecules used in this work. Structure in solution was extracted from a frame of the molecular dynamics simulations using Amber MD package¹ with ff99sb force field for the peptide². For each peptide, a water box was added (TIP3 waters³) and the simulation was performed for 20 ns at 300K.

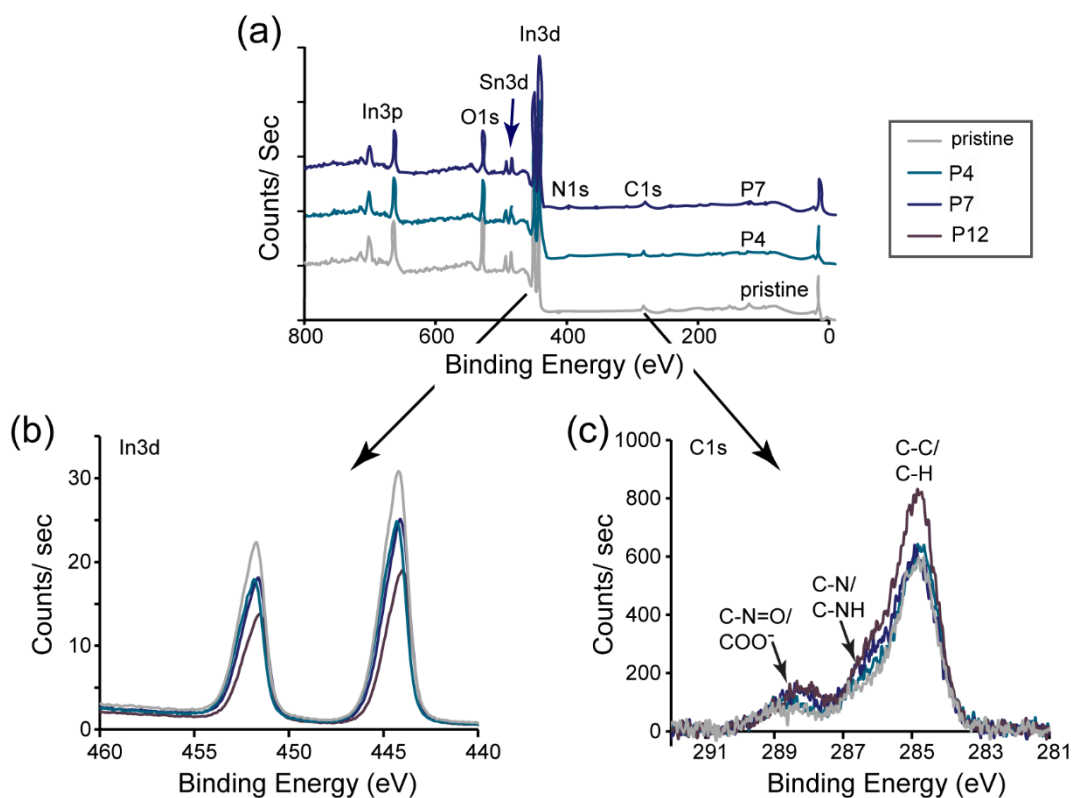


Figure S2. a) XPS survey spectra of Pristine ITO, and ITO functionalized with **P4**, and **P7**. b) High resolution XPS spectra of the In3d peak which was used for coverage calculations. c) High resolution XPS spectra of the C1s peak.

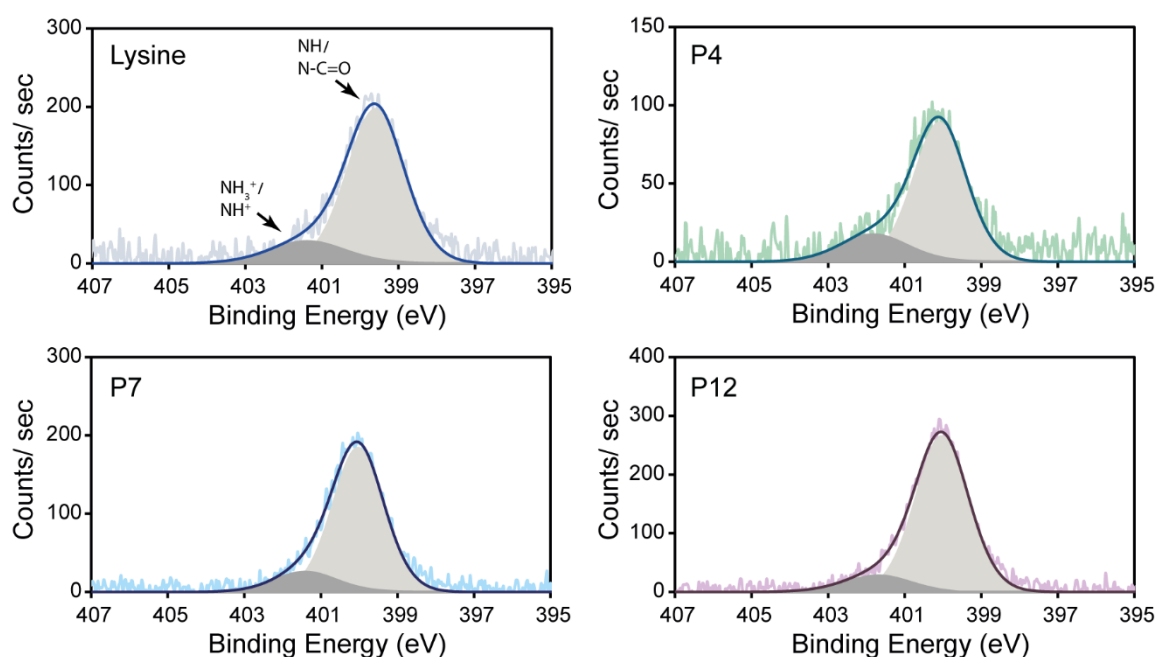


Figure S3. Deconvolution of the N1s peak obtained by high resolution XPS for monolayers of the three basic peptides and lysine.

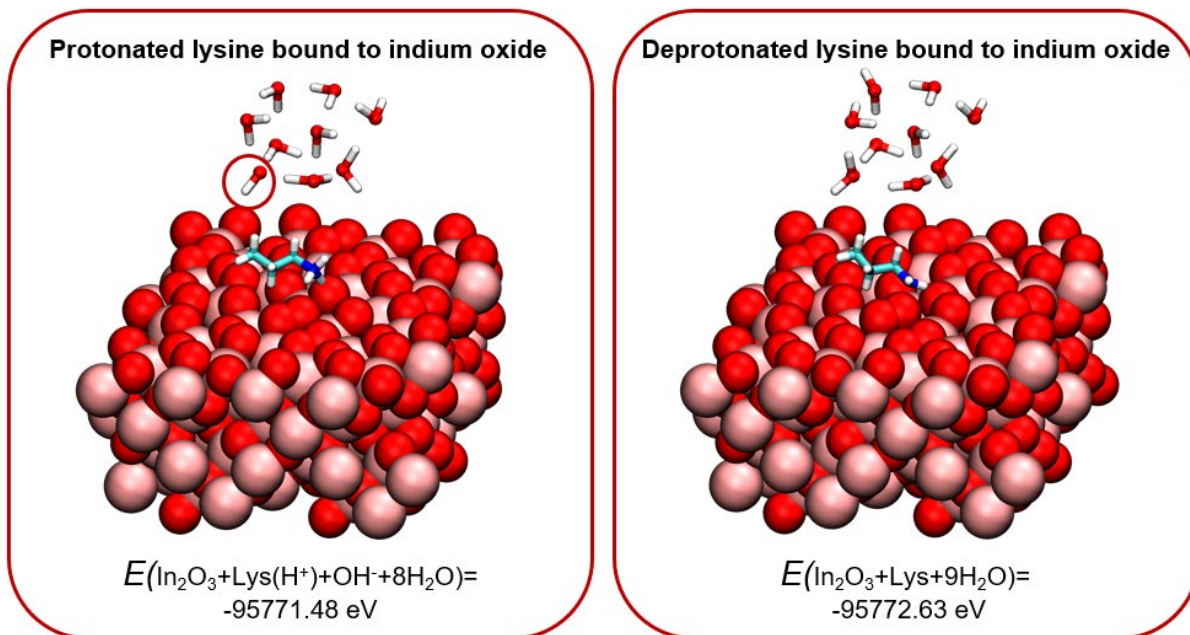


Figure S4. A model for the calculation of the energy of lysine bound to indium oxide in water. The model for the calculations consisted of a 20x20 nm² box with the amino acid in its deprotonated (right) or deprotonated state (left) on indium oxide surface. The water cluster contained nine water molecules (right) and eight water molecules and one OH⁻ (circled, left). For each of the systems, the geometry was relaxed and the energy was calculated using density functional theory (DFT) calculations.

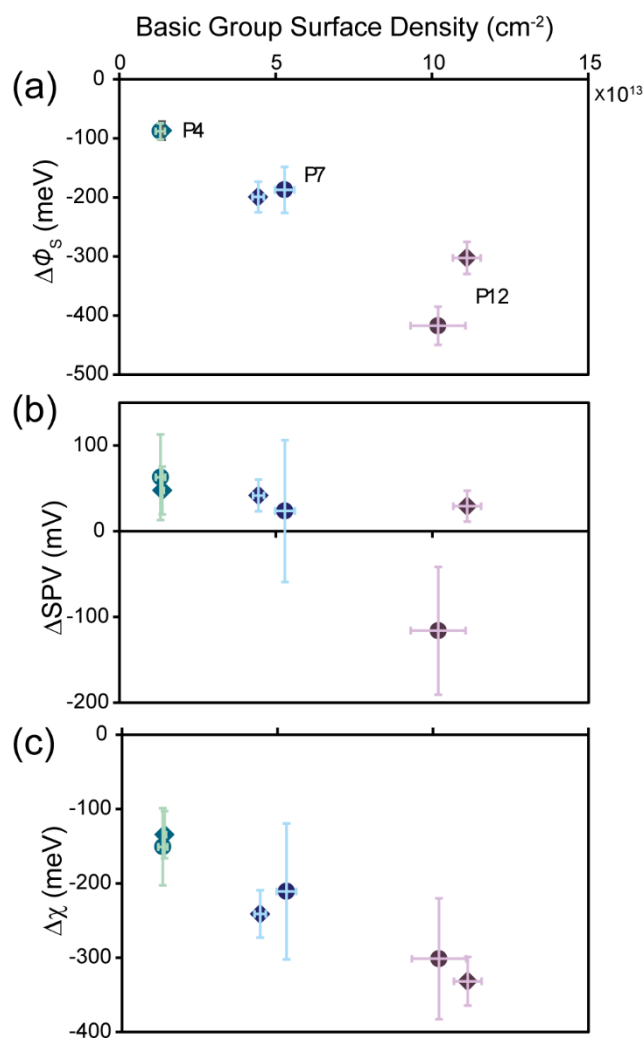


Figure S5. Effect of peptide assembly on surface electronic properties of ITO, for both assembly solution concentrations 0.5 and 2 mM. a) Change in the work function with respect to pristine ITO substrate. b) Change in the SPV with respect to pristine ITO substrate upon illumination with 18 mW laser, at a wavelength of 375 nm. c) Change in the electron affinity with respect to pristine ITO substrate, calculated as $\Delta\chi = \Delta\phi_s - \Delta SPV$.

Table S1. Analysis of AFM topography images.

	Maximum Height [nm]	Average Height [nm]	Roughness [nm]
Pristine ITO	16.4	8.2	1.4
P4	19.1	12.4	1.4
P7	20.6	12.3	1.6
P12	20.0	10.9	1.7

Table S2. Evaluation of primary amine protonation. Atomic % of protonated species of nitrogen was derived from high resolution XPS measurements of the N1s peak after deconvolution. The percent of primary amines was evaluated from the peptide sequence as the number of primary amines divided by the number of basic groups and amide groups in the sequence. The ratio of these two quantities provides the fraction of protonated primary amines.

	% Protonated Nitrogen	% Primary amines in the sequence	%Protonation
P4	18±1	10	>100*
P7	12±1	22	54
P12	12±1	28	43

*A protonation level above 100% may reflect a larger error since the nitrogen peak is overall smaller due to lower surface coverage. Alternatively, it may suggest contribution of protonated imidazole groups to the XPS peak of the protonated amine for P4.

References

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