Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Electronic structure of dipeptides in the gas-phase and as an adsorbed monolayer

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Possible near-degenerate configurations of 2Ala in gas-phase:

We considered several configurations of 2Ala with varying ψ and φ torsion angles and theoretically optimized the ensuing structures. Figure S1 shows such different combinations of ψ and φ, along with the corresponding total energy.

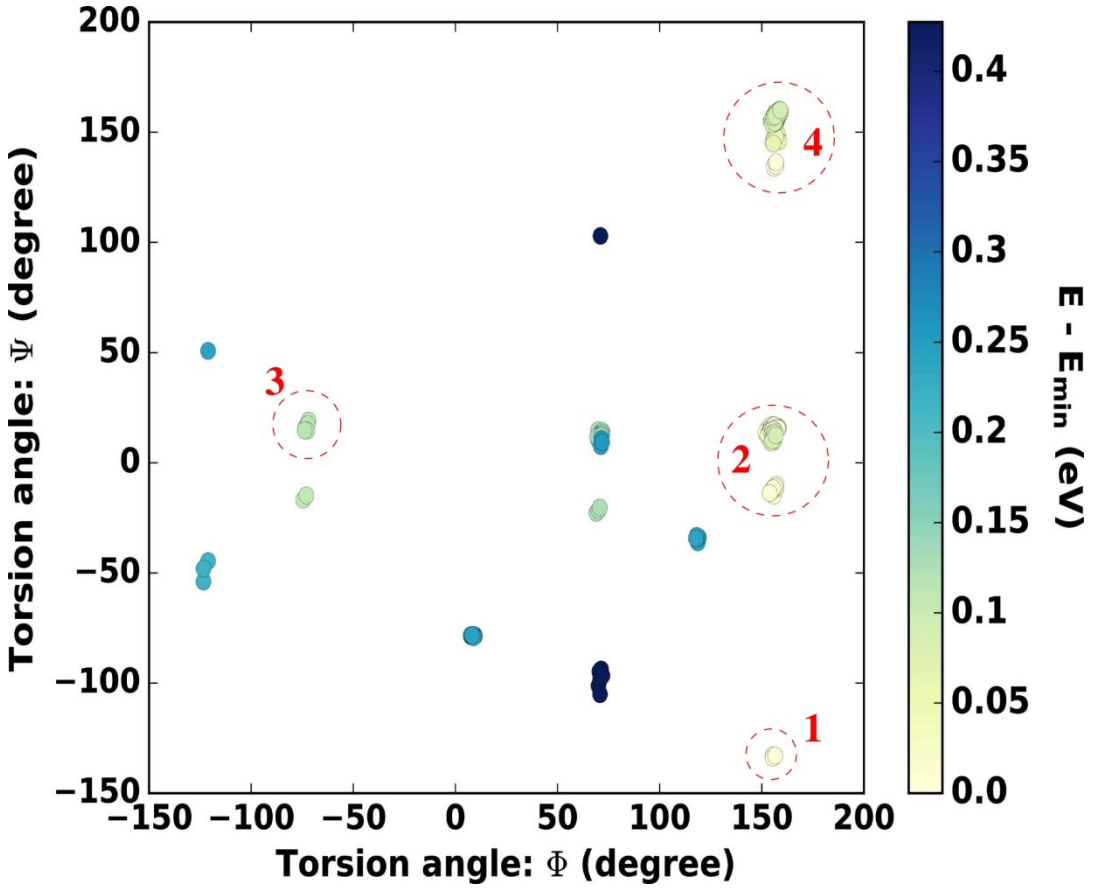

Figure S1. Combinations of torsional angles ψ and φ for different theoretically-optimized conformations of 2Ala. The associated color bar indicates the total energy of individual conformations, considering the lowest energy found as the zero of the scale. The dashed, red-encircled regions represent conformations that are very close to the minimum energy conformation (which is indicated as 1).

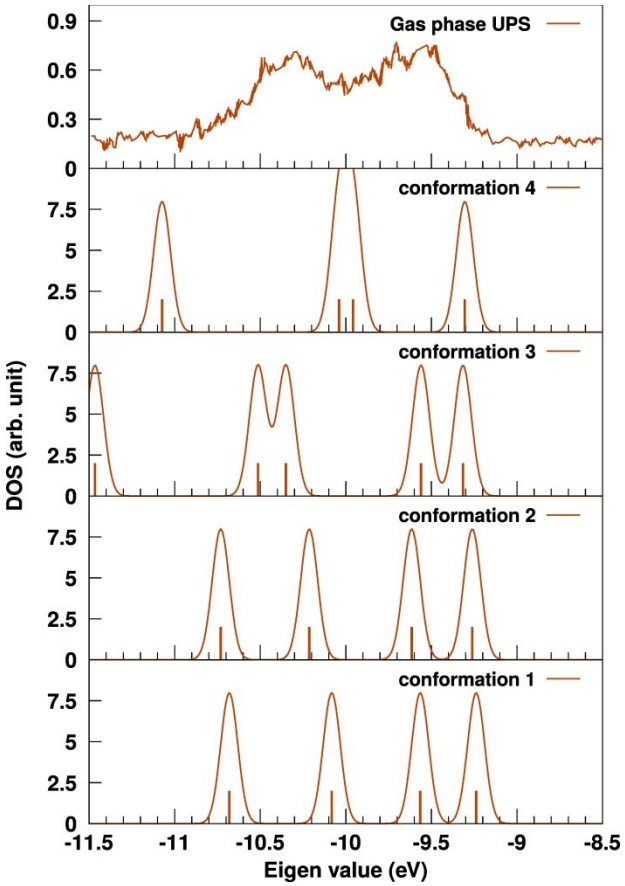

Figure S2. Comparison of experimental and simulated gas-phase UPS data for different conformations of 2Ala, with the conformation number taken from Figure S1. Conformation 3 shows the best agreement with the experimental spectrum and was used to generate the data shown for gas-phase 2Ala in the main text.

Ellipsometric measurements to determine the thickness of MPA-dipeptide monolayer

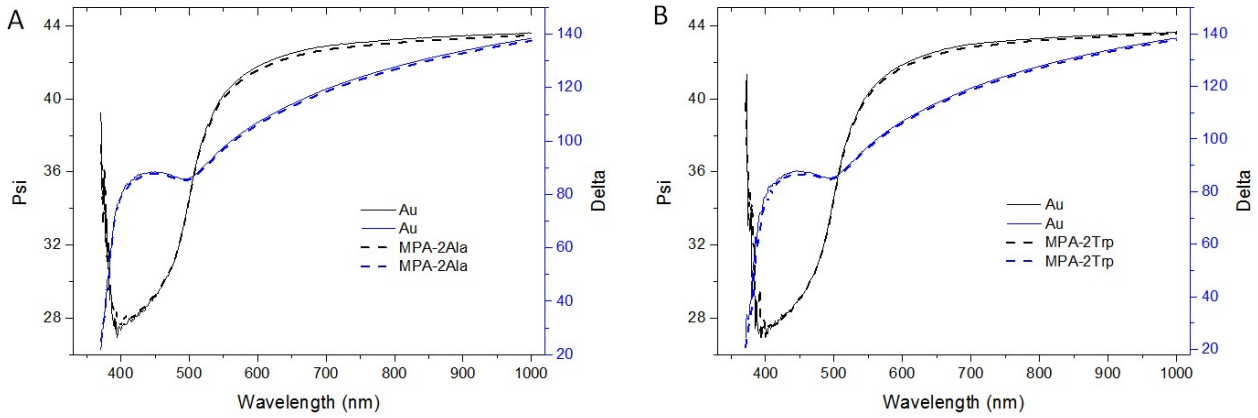

Figure S3. The "psi" and "delta" spectra of bare Au and MPA-dipeptide monolayers on Au substrate. A) Au substrate and MPA-2Ala, B) Au substrate and MPA-2Trp.

If we fit a bare Au spectrum with the Cauchy model, instead of the MPA-dipeptide monolayer, we will obtain 0 for thickness. This indicates that the monolayer thickness from Ellipsometry is acceptable.

Schematic electronic structure diagram:

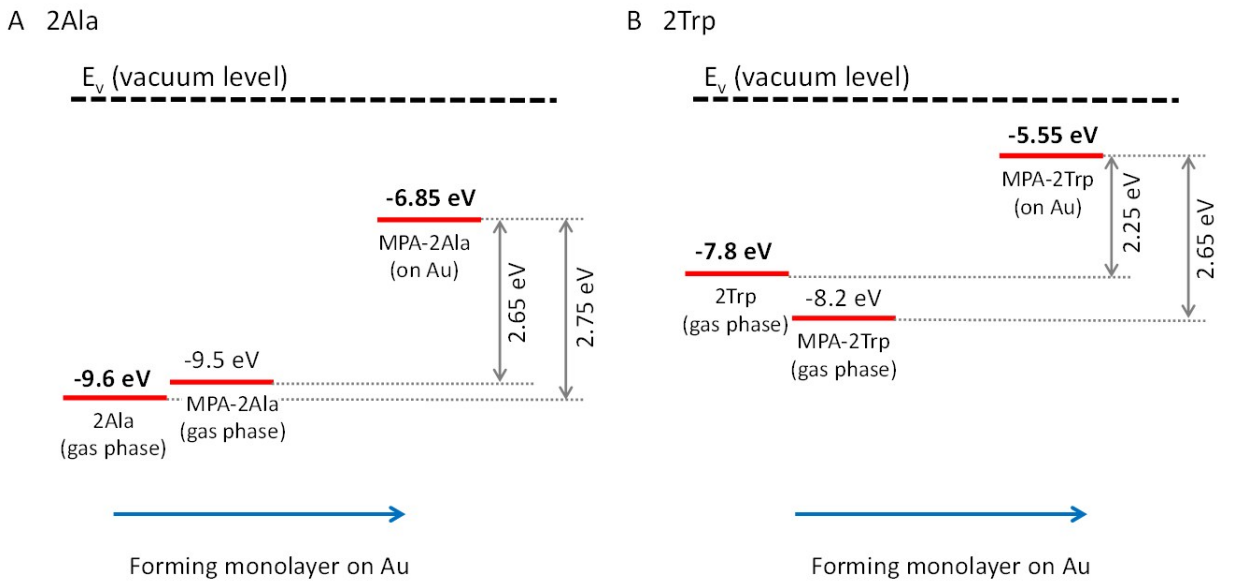

Figure S4. Schematic diagram of energy level changes from the gas-phase dipeptide to the MPA-dipeptide monolayer on the Au surface: A) 2Ala, B) 2Trp. The IPs of dipeptides in the gas-phase and of the MPA-dipeptides on Au are measured experimentally. The IPs of MPA-dipeptides in the gas phase could not be measured; the values, used here, are obtained from the experimentally measured gas-phase values for the dipeptides, modified by the difference between calculated IP values for the dipeptide and the MPA-dipeptide in the gas phase.