Supporting Information

Maria Hoernke[1] , Jessica A. Falenski[2] , Christian Schwieger[3 4] , Beate Koksch[2] and Gerald Brezesinski[1] *

Triggers for β-Sheet Formation at the Hydrophobic-Hydrophilic Interface: High Concentration, In-Plane Orientational Order, and Metal Ion Complexation

Calculation of the size of a peptide of 26 amino acid residues in different conformations

width x length = area

width x height x length = volume

elongated α-helix: 17 Åx 40 Å= 680 Å^2 = 6.8 nm^2

17 Åx 17 Åx 40 Å= 11 560 Å^3

elongated β-sheet:

5 Åx 85 Å= 425 Å^2 = 4.25 nm^2

5 Åx 10 Åx 87 Å= 4350 Å^3 = 4.35 nm^3

A β-sheet takes up 2/3 of the lateral space of an α-helix.

The peptides contain $\approx$ 1700 eletrons

maximum surface concentration:

helix 140 mM

sheet: 370 mM

[1]MPIKG
[2]FU Berlin
[3]MLU
[4]INRA

Calculation of the maximum surface concentration (2D) of a peptide of 26 amino acid residues in different conformations

Surface concentration (2D):

width x height x length = volume –> concentration

β-sheet: 0.4 nm x 1 nm x 5 nm –> 0.370 M = 370 mM

α-helix: 1.7 nm x 1.7 nm x 4 nm –> 0.140 M = 140 mM

Time dependent conformational behaviour of i,i+1 and i,i+7 in bulk

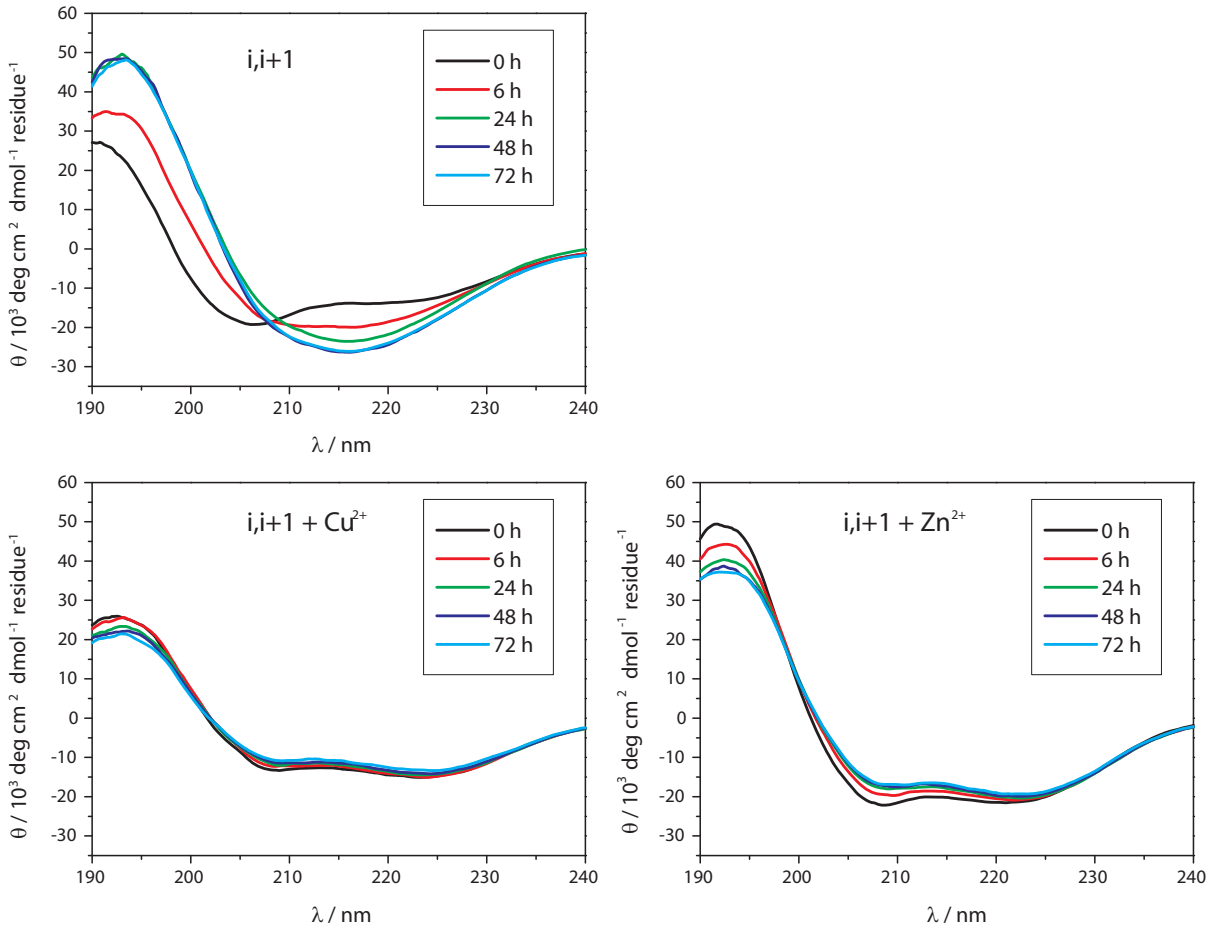

Figure S 1: CD spectra of i,i+1 and Cu^{2+} (90 μM, 10 mM phosphate buffer, pH 7.4)

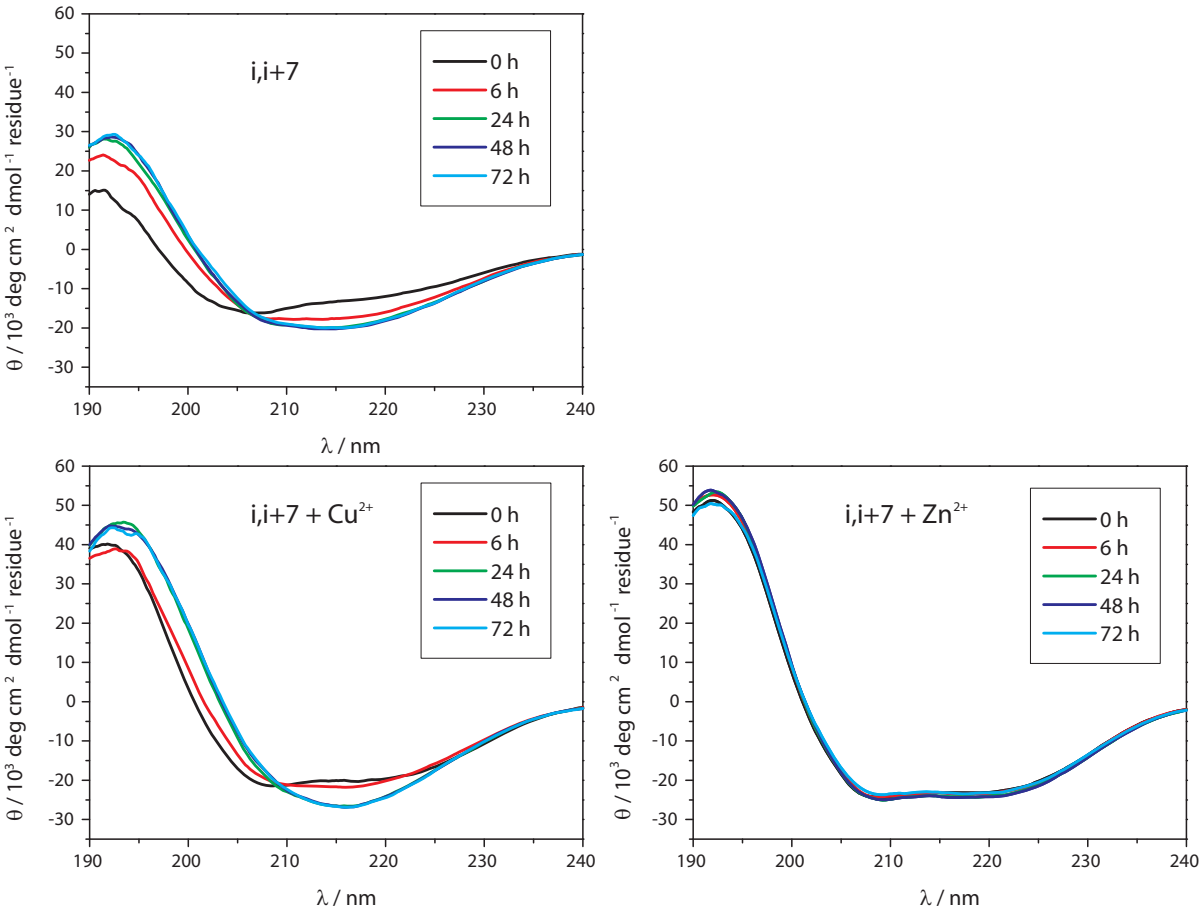

Figure S 2: CD spectra of i,i+7 and Zn^{2+} (90 μM, 10 mM phosphate buffer, pH 7.4)

Angle Dependent Measurements to Decide on the Presence of α-Helices

Only in angle dependent measurements, the bands arising from an α-helical conformation or the unfolded conformation become distinguishable. The band position of the amide I vibration of unfolded peptide is ≈ 1645 cm^{-1} and has a high full-width at half-maximum (FWHM). The amide I band of α-helical peptides is found at higher wavenumbers (≈ 1655 cm^{-1}).[43] When recorded with p-polarized light and angles of incidence below and above the Brewster angle, additionally, the amide II vibrational band of α-helices changes its sign. Together, the amide I band position and inversion of the amide II sign, indicate that the band at ≈ 1655 cm^{-1} found in the spectra taken at equilibrium surface pressure (for example Figure 3 B) is arising from α-helices and not from unfolded peptides in layers of i,i+1 and i,i+7 (data not shown). Even though, the amide region of all spectra could be satisfactorily simulated and fitted assuming the presence of α-helices only, it cannot be totally precluded, that bands of unfolded peptide structures overlap. Similarly, shortly after the beginning of adsorption, i,i+4 layers clearly contain α-helical peptides, independent of the presence of metal ions.

Time dependent conformational behaviour of i,i+1 and i,i+7 at the air-water interface

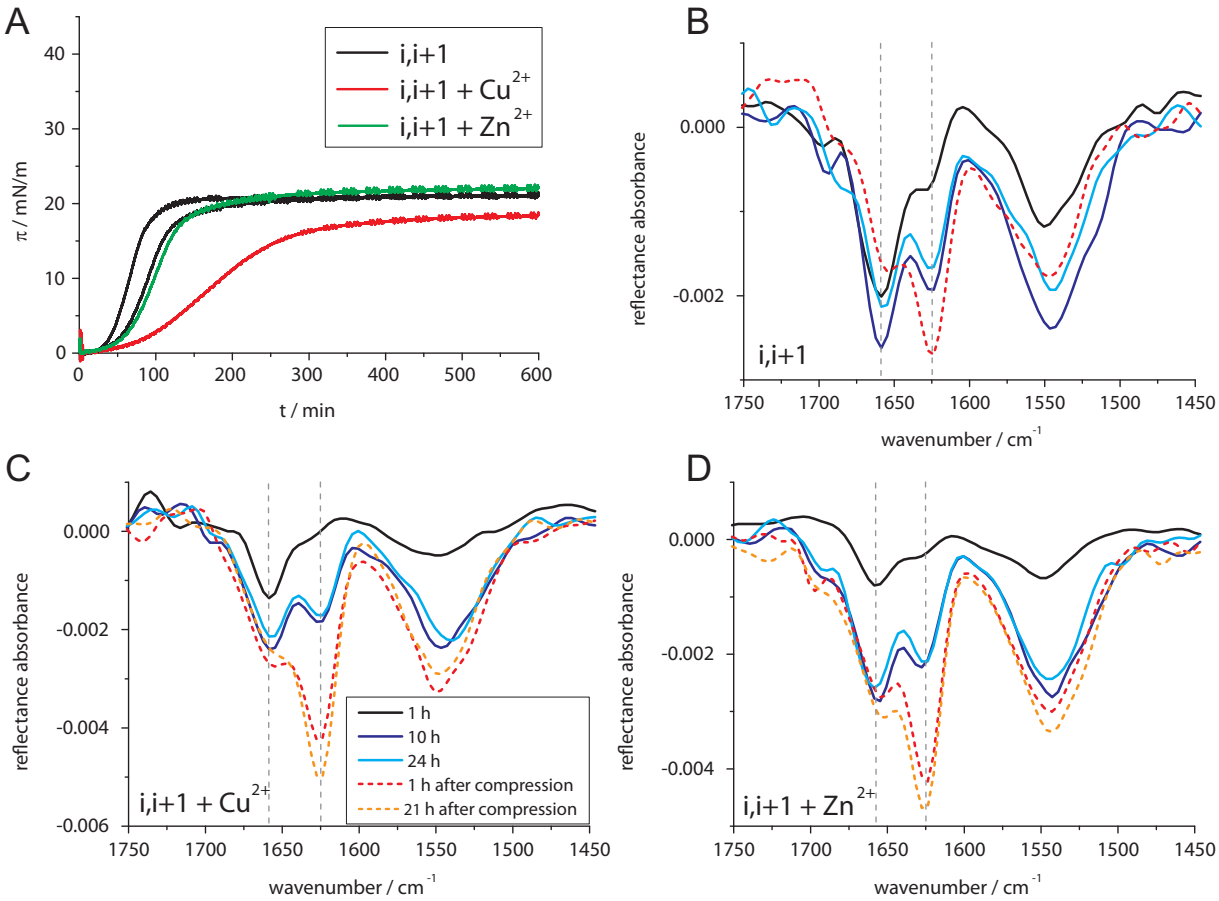

Figure S 3: A π-t adsorption isotherm of i,i+1 B, C and D time dependent and surface pressure dependent IRRA spectra of i,i+1. Grey lines indicate the wavenumbers of bands at 1655 cm^{-1} assigned to α-helix and 1625 cm^{-1} assigned to β-sheet. (0.3 μM) at the air-water interface, 10 mM PBS, pH 7.4, 150 mM NaCl, 20 °C.

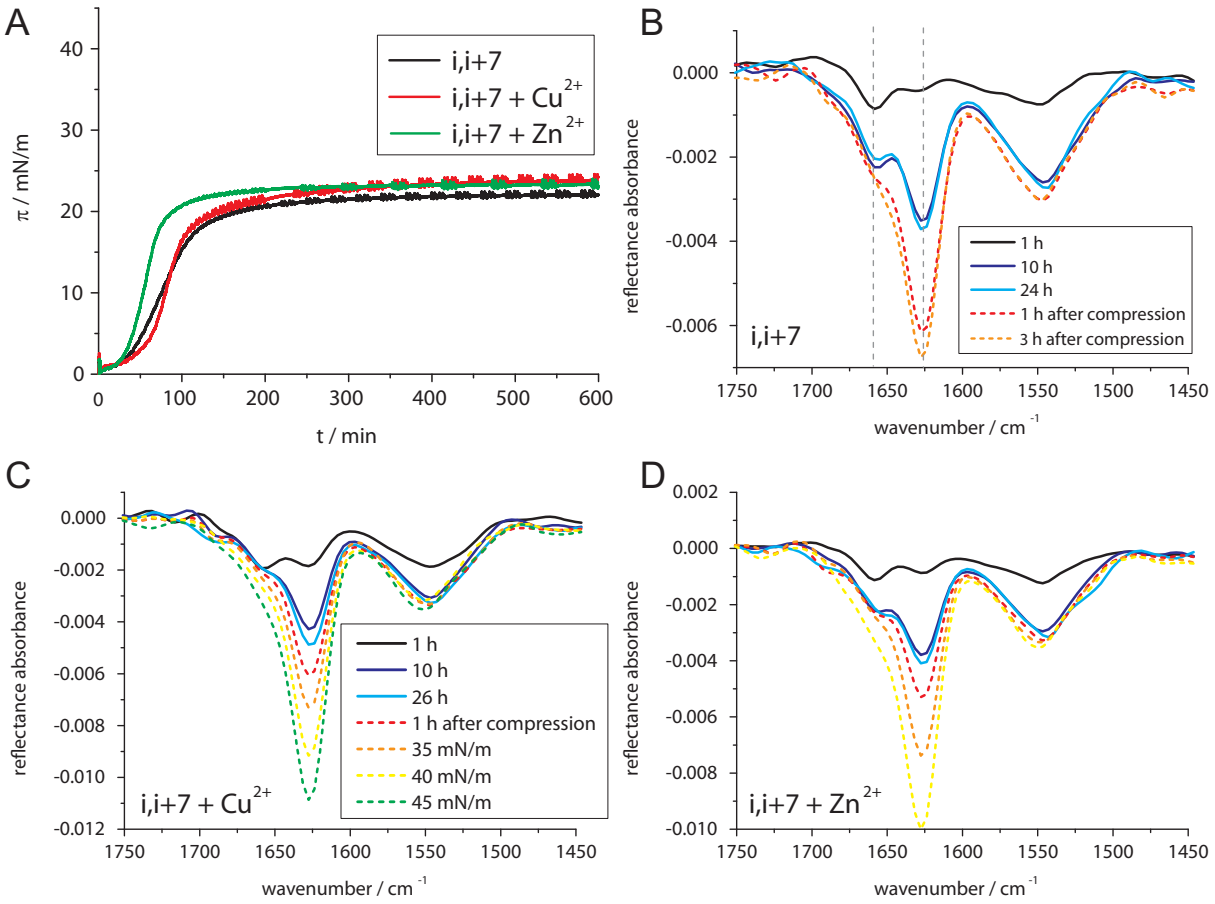

Figure S 4: A π-t adsorption isotherm of i,i+7 B, C and D time dependent and surface pressure dependent IRRA spectra of i,i+1. Grey lines indicate the wavenumbers of bands at 1655 cm^{-1} assigned to α-helix and 1625 cm^{-1} assigned to β-sheet. (0.3 μM) at the air-water interface, 10 mM PBS, pH 7.4, 150 mM NaCl, 20 °C.

IRRAS Simulation Details

Table 2: IRRAS simulation data: Peak positions and tilt angles. Peak positions are indicated in the table, except for the footnotes. (10 mM PBS, 150 mM NaCl at 20 C. The peptides concentration in the bulk phase was 0.3 μM before adsorption.)

Peptide	condition	no Metal		Cu^{2+}		Zn^{2+}	
		ν		ν		ν	
i,i+1+7		1656					
	π_{eq}	90°					
	π_{eq} 20 h	90° - 88°					
	30 mN/m	90° - 89°	0°				
i,i+1		1655	1625	1655	1625	1655	1625
	π_{eq}	90°	0°	90°	0°	90°	0°
	30 mN/m	90°	0°	90°	0°	90°	0°
i,i+7		1655	1625	1655	1625	1655	1625
	π_{eq}	90° - 89°	0°	90°	0°	90°	0°
	$\pi_{eq} \approx$ 24 h	90° - 88°	0° - 2°	90° - 84°	0°	90° - 89°	0° - 1°
	30 mN/m	90°	0°	90° - 85°	0°		
	35 mN/m			90°	0°	90°	0°
	40 mN/m			90°	0°	90°	0°
	45 mN/m			90°	0°		
i,i+4		1656	1625	1656	1625	1656	1625
	π_{eq}	90°	–	90° - 64°	0° - 18°	90° - 74°	0° - 21°
	$\pi_{eq} \approx$ 10 h	90	0	90° - 68° [a]	0° - 5°	90° [b]	0°
	30 mN/m			90° - 84° [c]	0°	–	0°
i,i+2		1656	1625	1656	1625	1656	1625
	π_{eq}	90° - 60°	–	90° - 66°	0° - 5°	–	0° - 31°
	$\pi_{eq} \approx$ 24 h	90° - 63° [d]	0° - 45°	90° - 50°	0° -28°		
	30 mN/m	–	0° - 5°	90° [e]	0°	–	0°

[a] 1653-1650
[b] 1649
[c] 1652
[d] 1651
[e] 1646 - 1658

Material and Methods

Concentration Determination for Circular Dichroism (CD) Measurements

Peptide concentrations were estimated by UV spectroscopy using the absorption maximum at 320 nm of o aminobenzoic acid (Abz), which was attached to each N terminus. A calibration curve was recorded using different concentrations of H_2N-Abz-Gly-OH HCl. After concentration determination peptide solutions were diluted to yield 90 μM peptide.

Circular Dichroism

Peptides were dissolved in phosphate buffer (90 μM peptide and 90 μM Cu^{2+} or Zn^{2+}, respectively, 100 mM phosphate buffer, pH 7.4). CD-spectra were recorded on a Jasco-715 spectropolarimeter at 20 °C using 0.1 cm Quartz Suprasil cuvettes (Hellma). Elipticity was normalized to concentration (c/mol L^{-1}), number of residues (n = 27, including the N terminal label Abz) and path length (l/cm) using

$$[\theta] = \frac{\theta_{obs}}{10000lcn}$$

where θ_{obs} is the measured ellipticity in millidegrees and $[\theta]$ the mean residue ellipticity given in 10^3 deg cm^2 $dmol^{-1}$ $residue^{-1}$. All measurements were repeated three times and the average was calculated.