Electronic Supplementary Information (ESI) for:

Interactions of aggregating peptides probed by IR-UV action spectroscopy

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List of Electronic Supplementary Information (ESI)

1. REMPI spectrum of Z-Ala-Ala-OMe (A)

The REMPI spectrum of Z-Ala-Ala-OMe shows two vibrational progressions starting at 37523 cm^{-1} (indicated with A-I, blue trace) and 37578 cm^{-1} (A-II, red trace).

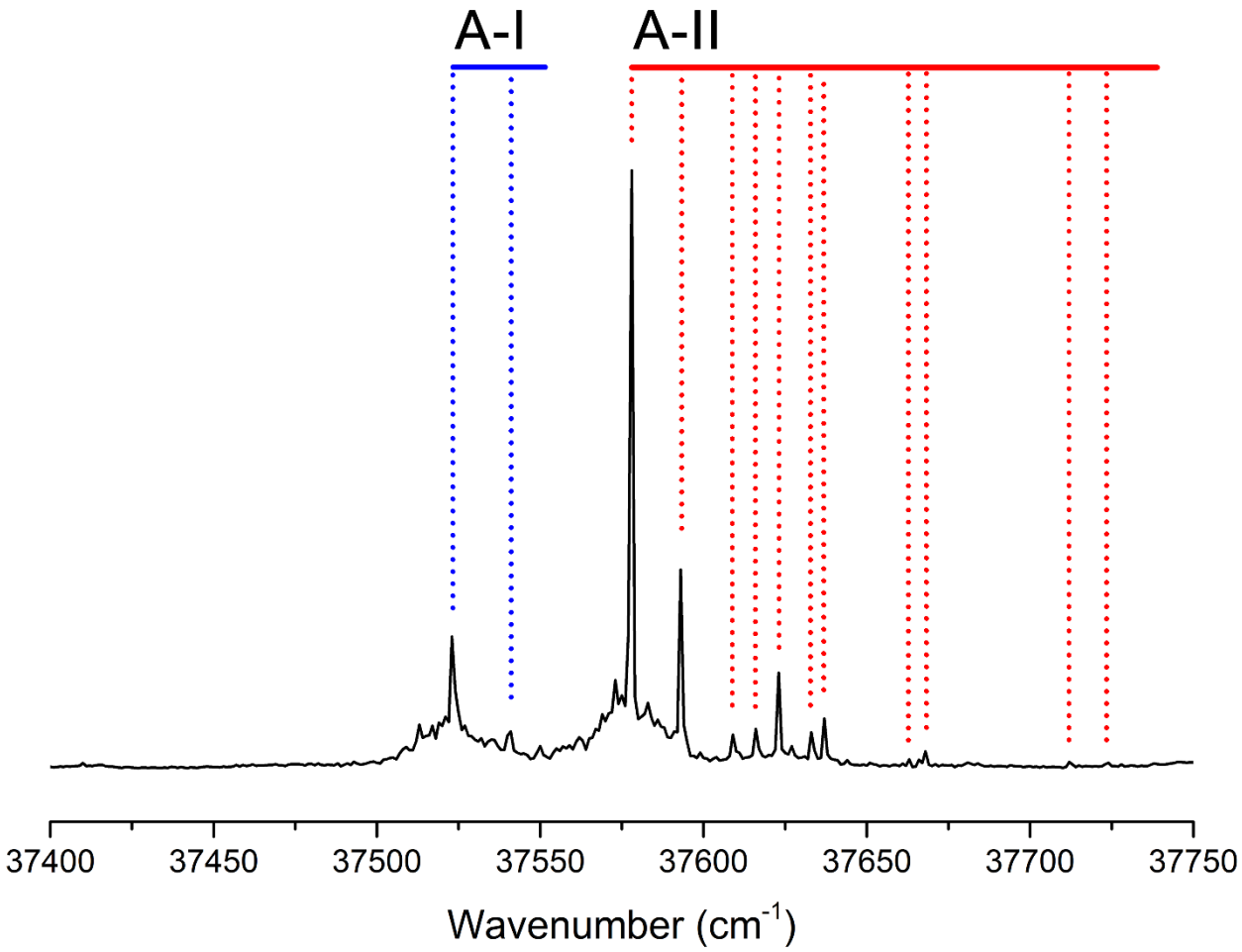


Figure SI.1: REMPI spectrum of the monomer of Z-Ala-Ala-OMe. Two conformers were identified using IR-UV hole-burning spectroscopy: A-I (blue) has its origin at 37523 cm^{-1} and A-II at 37578 cm^{-1}.

2. REMPI spectrum of Ac-Ala-Ala-OBn (B)

The REMPI spectrum of the monomer of peptide B (Figure SI.2) shows three main bands: At 37495 cm^{-1} (blue), 37530 cm^{-1} (asterisk *) and at 37551 cm^{-1} (red). The blue and red traces were shown to correspond to two separate conformers, named B-I and B-II. The peak indicated with the asterisk was previously determined to only apparent when using argon. This indicates that this peak is either due to kinetic trapping due to the argon, or because of a complex with argon, which is then fragmented upon photoionization. [1]

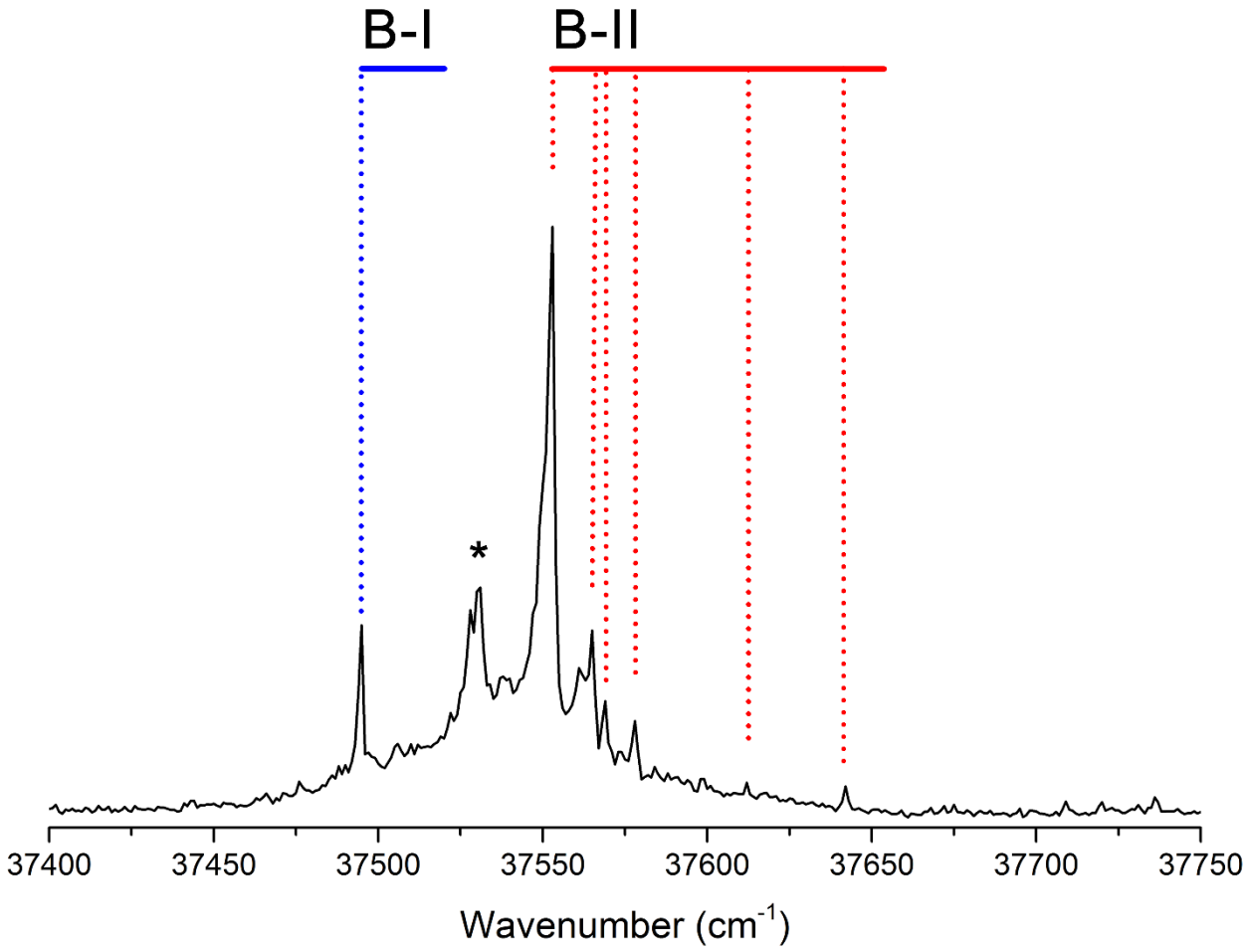


Figure SI.2: REMPI spectrum of the monomer of Ac-Ala-Ala-OBn. Two conformers were identified using IR-UV hole-burning spectroscopy: B-I (blue) has its origin at 37495 cm^{-1} and B-II (red) at 37550 cm^{-1}.

References:

1. E. Gloaguen, B. de Courcy, J.-P. Piquemal, J. Pilmé, O. Parisel, R. Pollet, H.S. Biswal, F. Piuzzi, B. Tardival, M. Broquier and M. Mons, *J. Am. Chem. Soc.*, 2010, **132**, 11860.

3. REMPI spectra of all dimers (AA, AB, BB, B3)

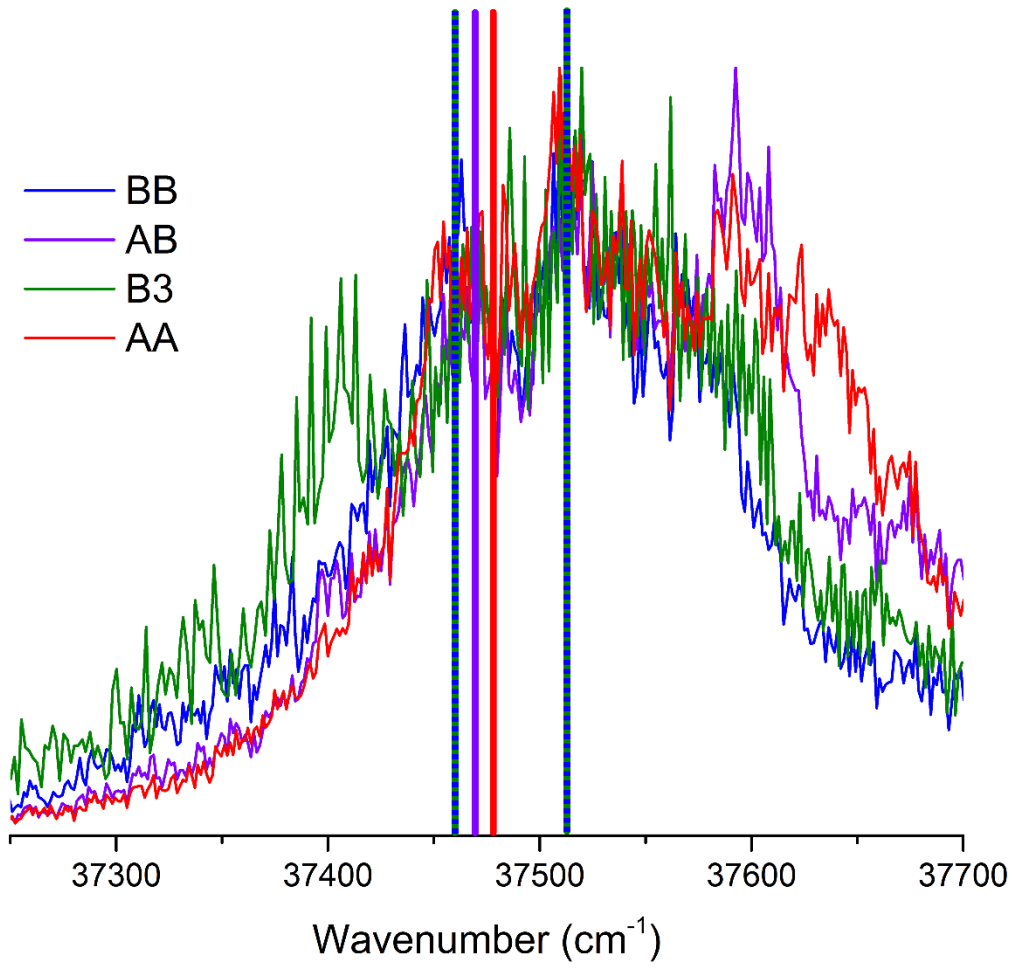


Figure SI.3: REMPI spectra of all measured dimers: Z-Ala-Ala-OMe (AA, red), Ac-Ala-Ala-OBn (BB, blue), their heterodimer (AB, purple), and the dimer of peptide B with Ac-Ala-Ala-Ala-OMe (B3, green). The lines indicate the position of the excitation laser at each infrared measurement. The infrared spectra of B3 and BB have both been obtained at 2 different wavelengths, hence the lines with two colors.

4. Mass spectrum

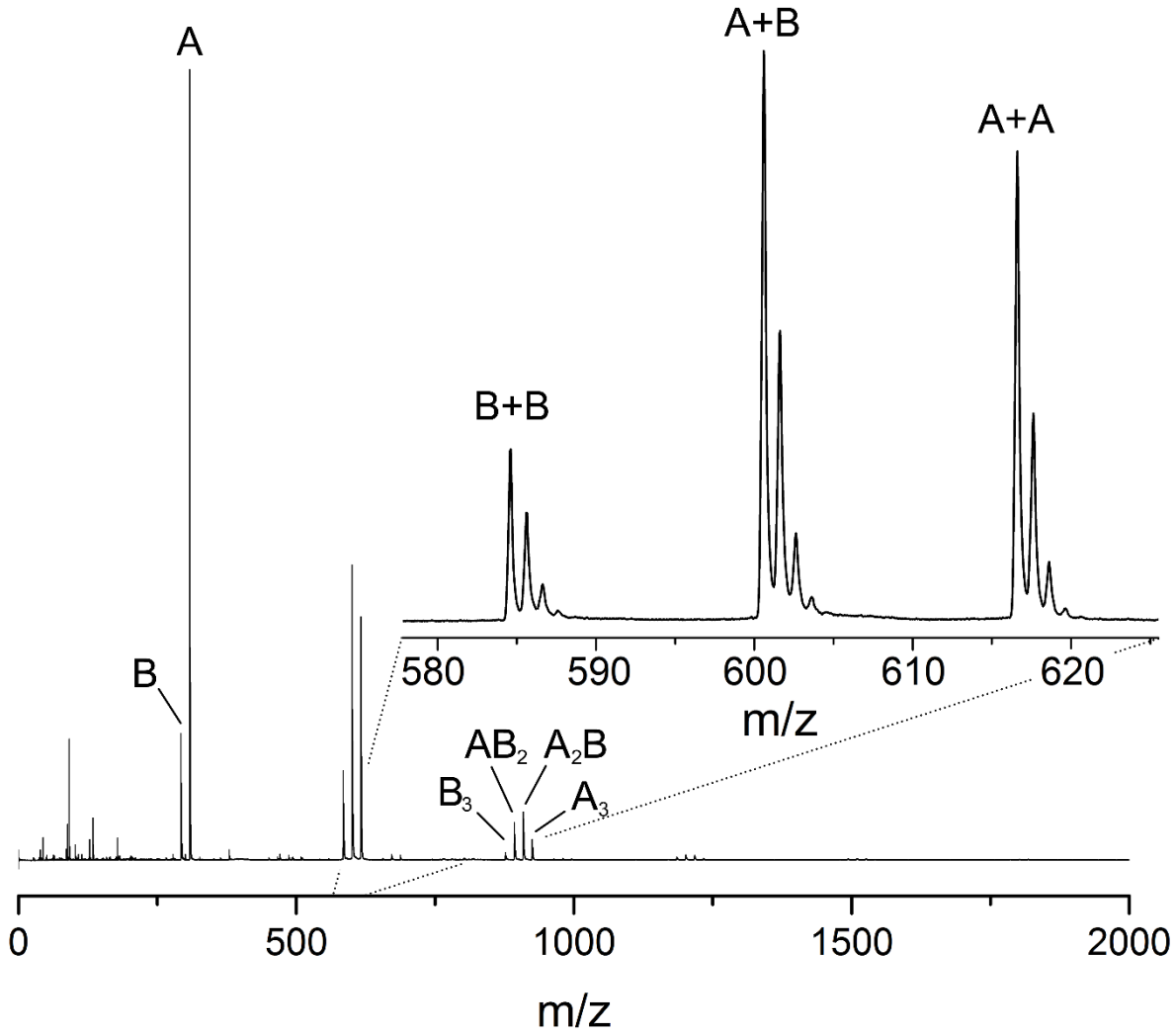


Figure SI.4: Mass spectrum of a mix of peptides A and B. The ratio between the two peptides in the monomer reflects the ratio of sample preparation (more of peptide A was put into the mixture). Visible are the monomers, dimers, trimers and tetramers.

5. Assignment peptide A dimer

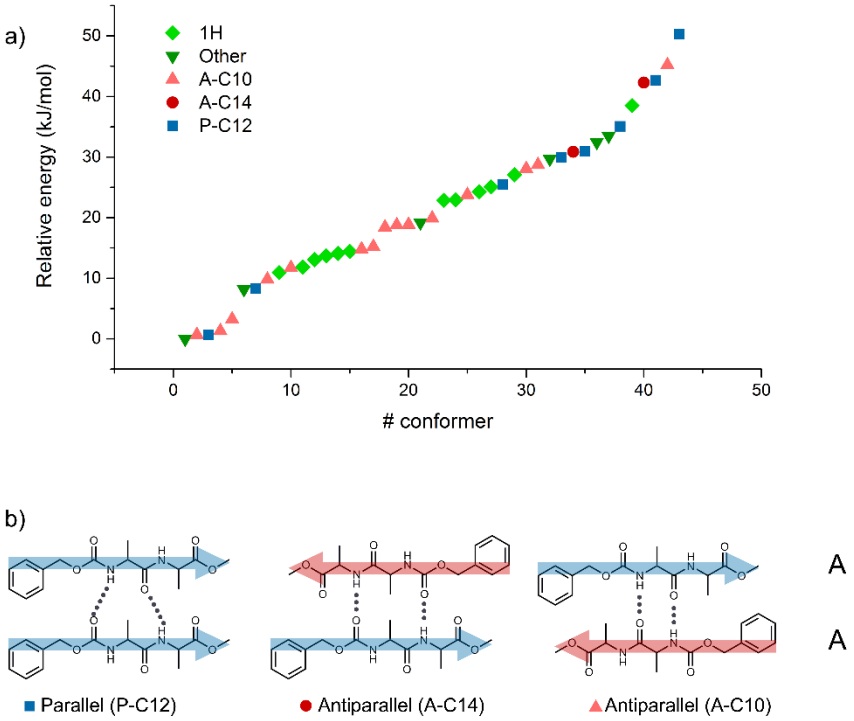
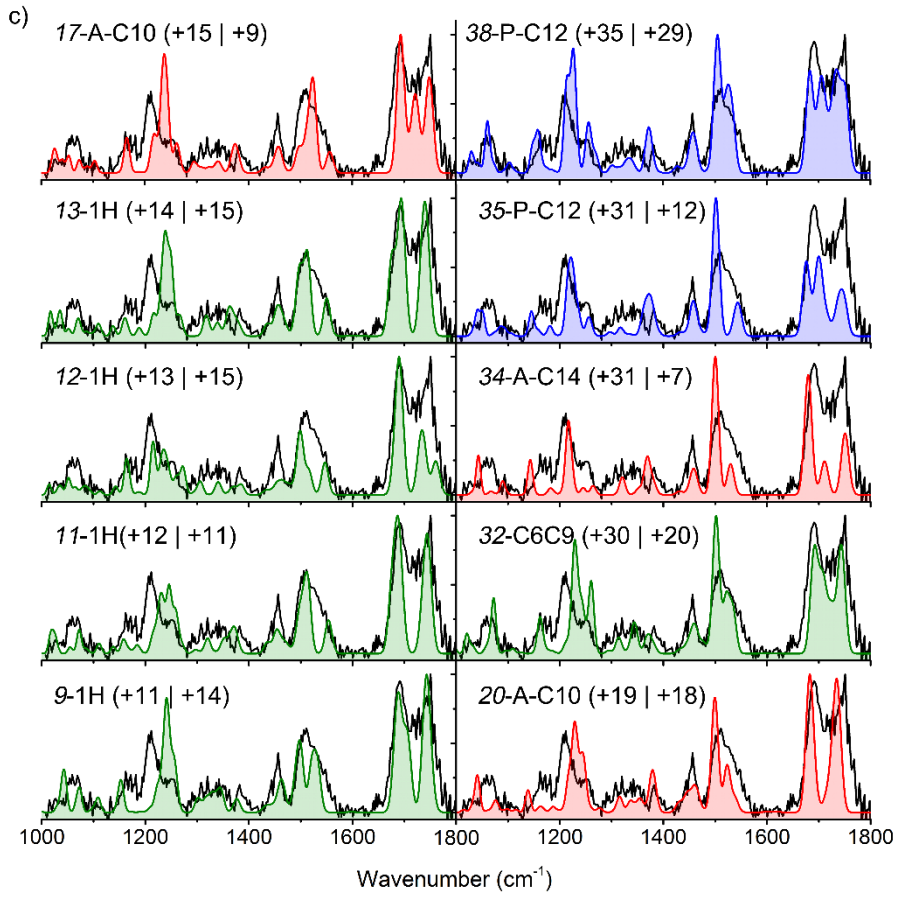
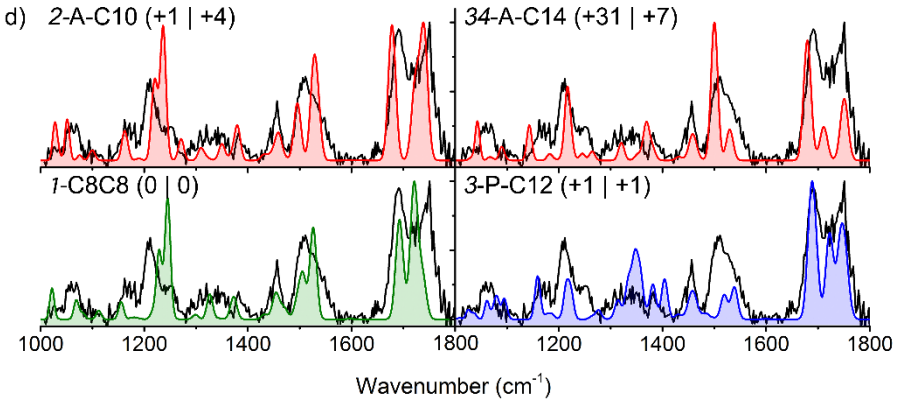
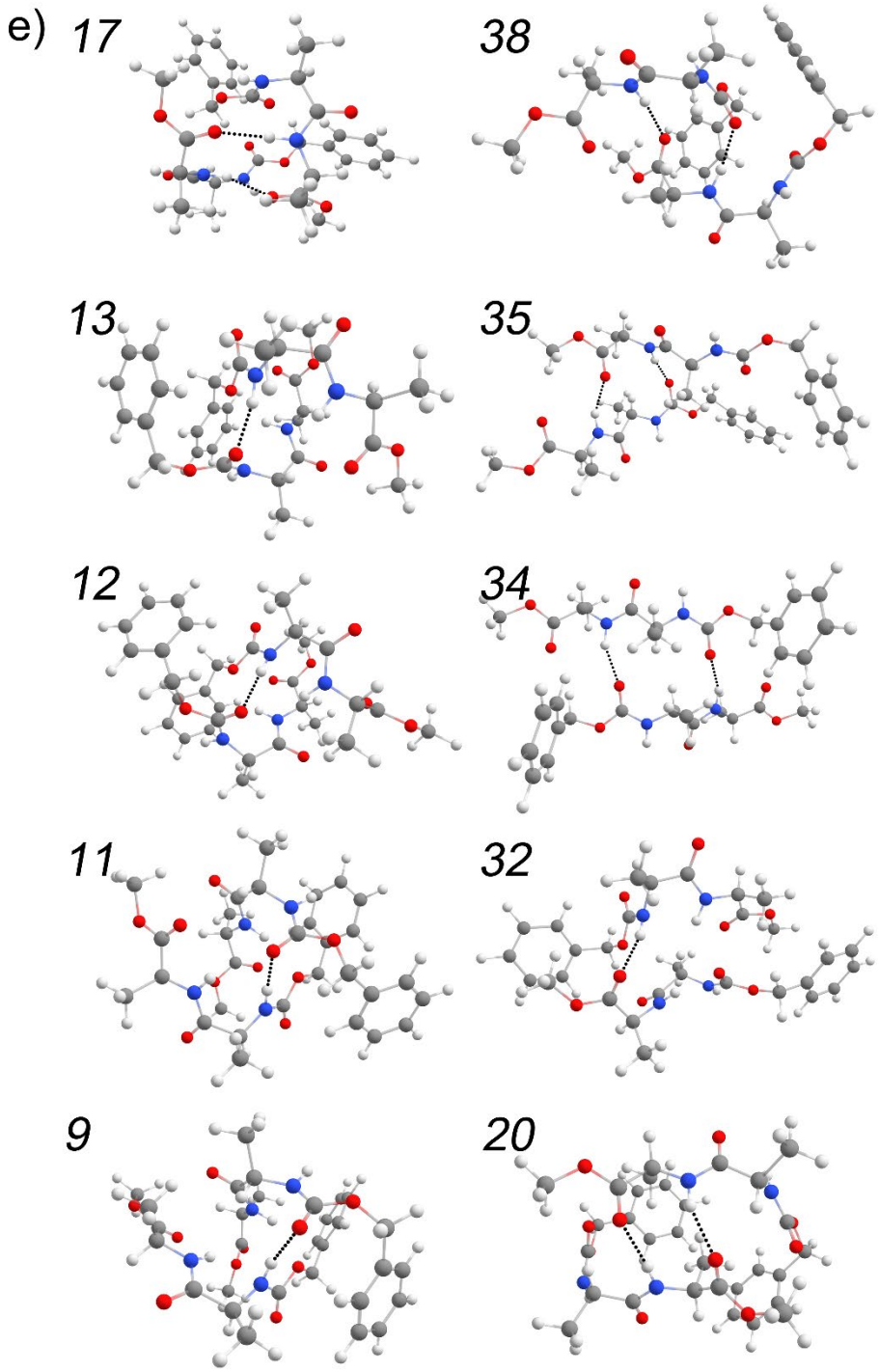


Figure SI.5: a) Relative zero-point corrected energies of all calculated conformers of the dimer of peptide A and their respective hydrogen bonding patterns: green diamant: singly hydrogen bonded dimer, green triangle: other structures with 2 hydrogen bonds, red triangle: anti-parallel C-10, red dot: anti-parallel C-14, blue cube: parallel C-10; b) Three possible hydrogen bond patterns, 1 parallel and 2 anti-parallel.

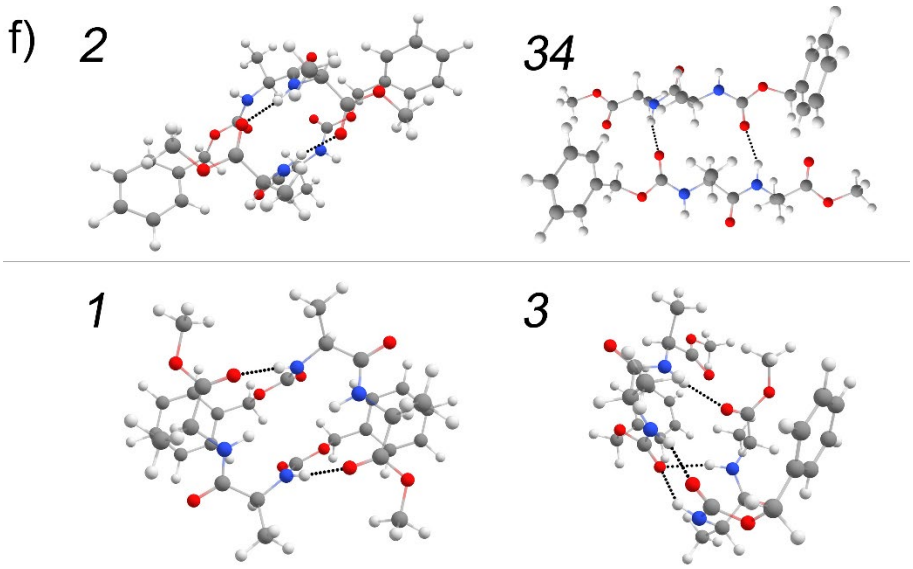




c) Infrared spectra of the ten lowest energy structures of dimer AA that have a reasonable overlap in the amide I and II region, with between brackets the relative energies in kJ/mol (zero-point corrected energy | With Gibbs free energy at 300K). d) Infrared spectra of the 4 lowest energy structures per family (Other, A-C10, P-C12 and A-C14).



e) Structures belonging to spectra of dimer AA shown in c)



f) Structures belonging to spectra of dimer AA shown in d)

6. Assignment peptide B+B dimer

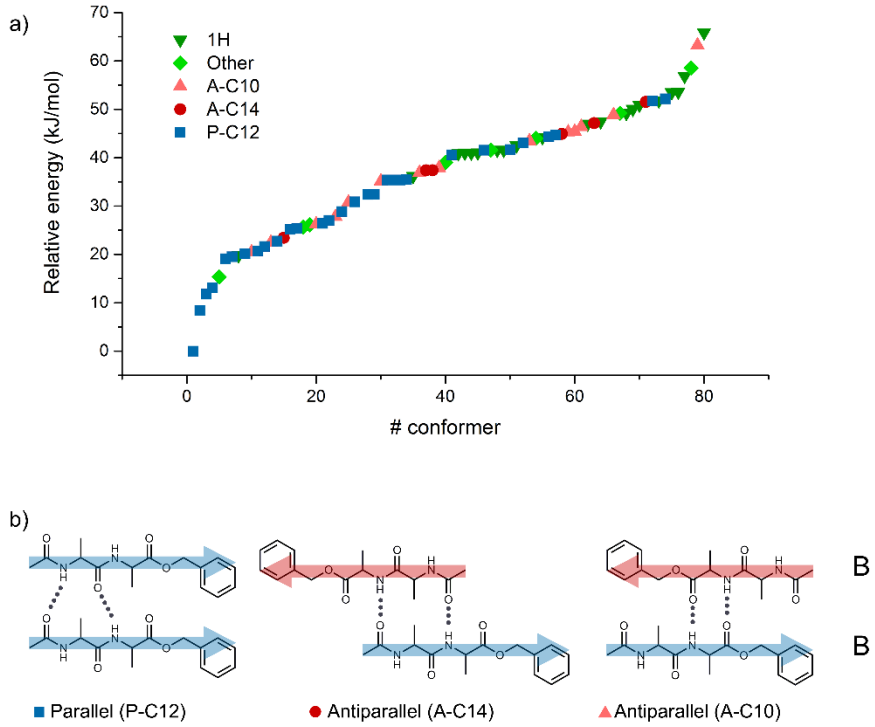
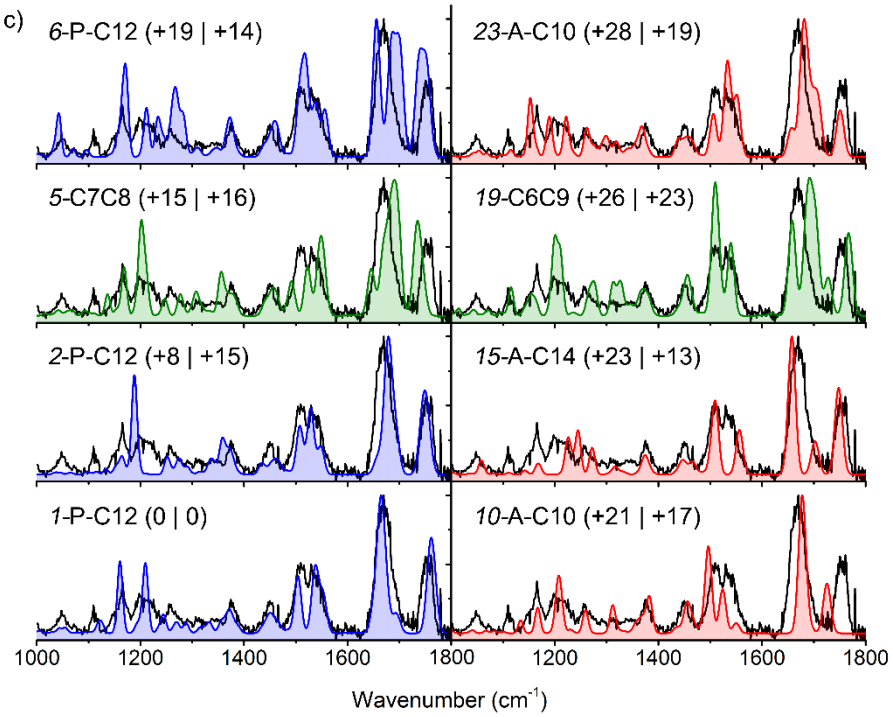
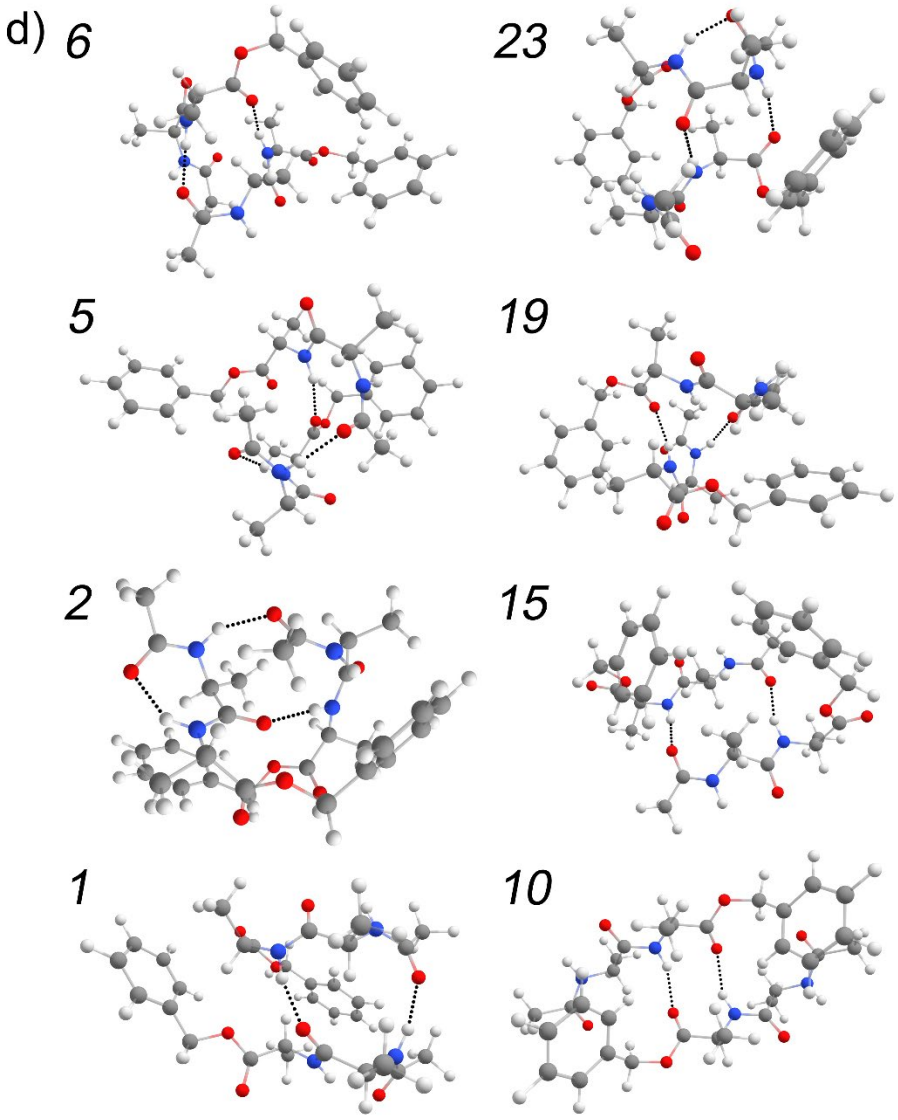


Figure SI.6: a) Relative zero-point corrected energies of all calculated conformers of the dimer of peptide B and their respective hydrogen bonding patterns: green diamant: singly hydrogen bonded dimer, green triangle: other structures with 2 hydrogen bonds, red triangle: anti-parallel C-10, red dot: anti-parallel C-14, blue cube: parallel C-10; b) Three possible hydrogen bond patterns, 1 parallel and 2 anti-parallel.



c) Infrared spectra of the eight lowest energy structures for each family of dimer BB, with between brackets the relative energies in kJ/mol (zero-point corrected energy | With Gibbs free energy at 300K).



d) Structures belonging to spectra of dimer BB shown in c)

7. Assignment peptide A+B dimer

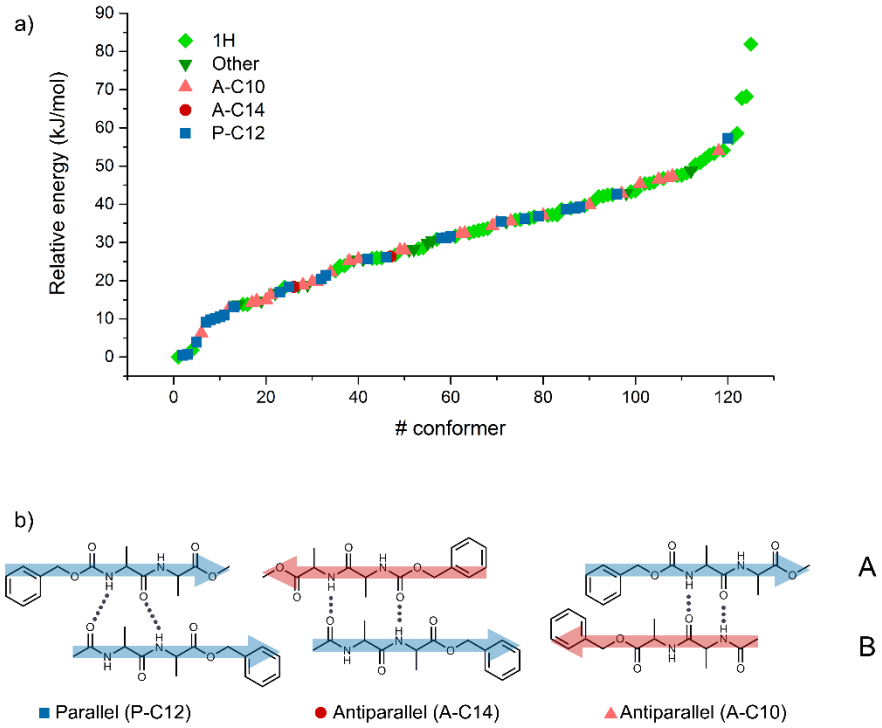
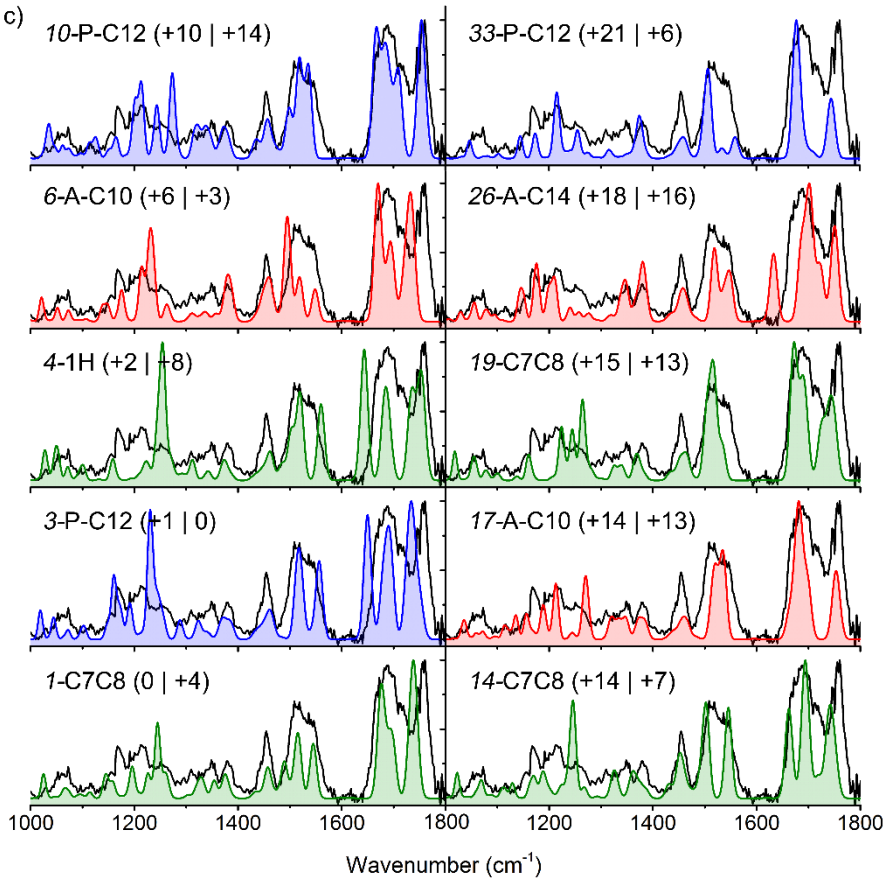
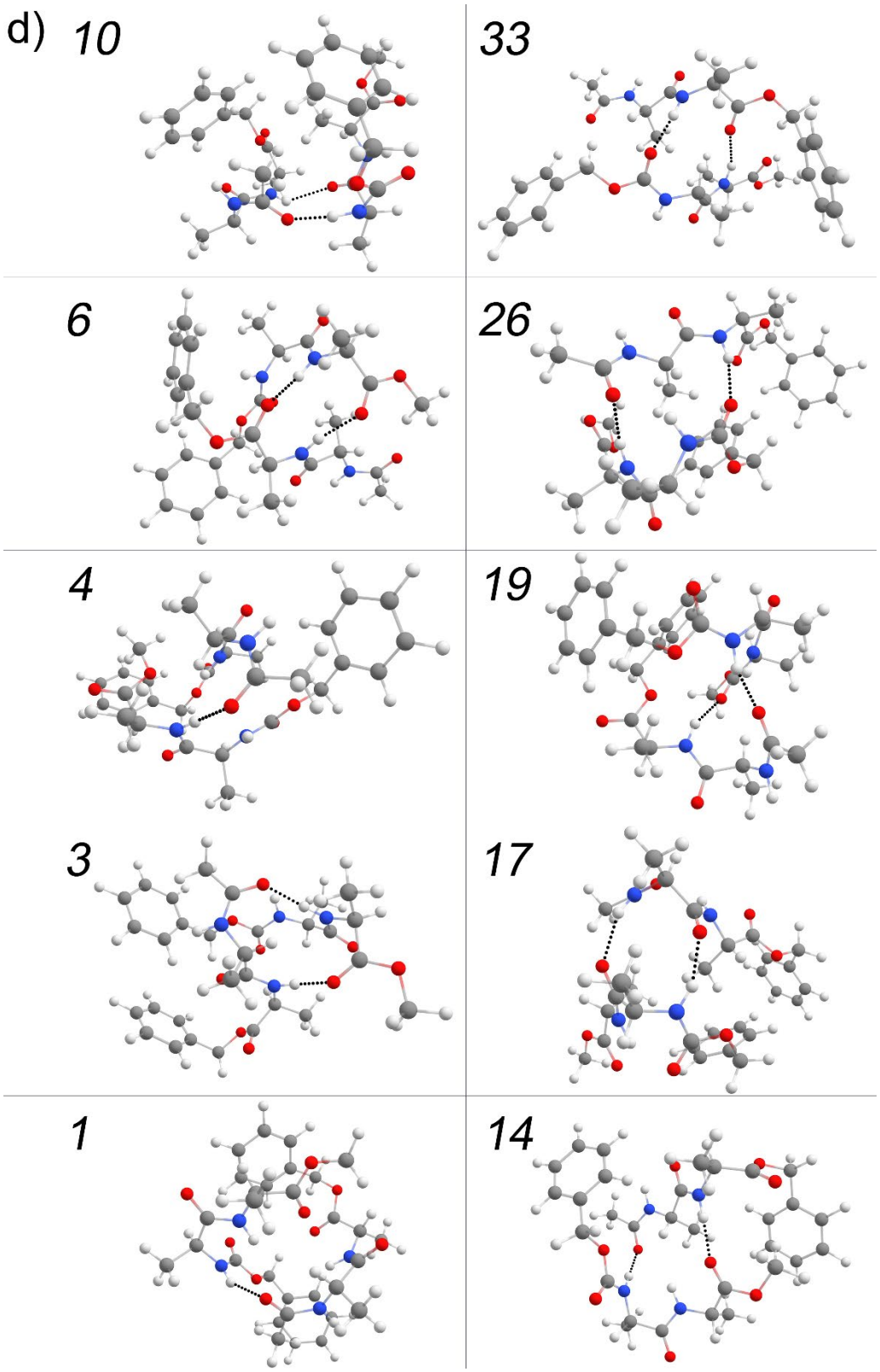


Figure SI.7: a) Relative zero-point corrected energies of all calculated conformers of the dimer of peptide A+B and their respective hydrogen bonding patterns: green diamant: singly hydrogen bonded dimer, green triangle: other structures with 2 hydrogen bonds, red triangle: anti-parallel C-10, red dot: anti-parallel C-14, blue cube: parallel C-10; b) Three possible hydrogen bond patterns, 1 parallel and 2 anti-parallel.



c) Infrared spectra of the ten lowest energy structures for each family of dimer AB, complemented with (higher energetic) good fitting spectra, with between brackets the relative energies in kJ/mol (zero-point corrected energy | With Gibbs free energy at 300K).



d) Structures belonging to spectra of dimer AB shown in c)

8. Assignment peptide B+3 dimer

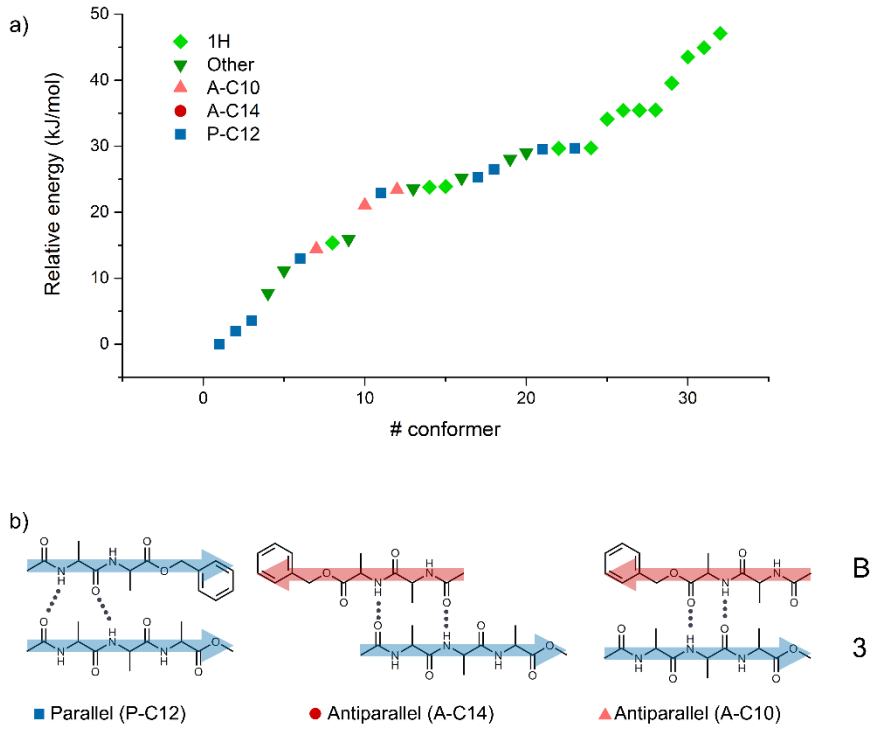
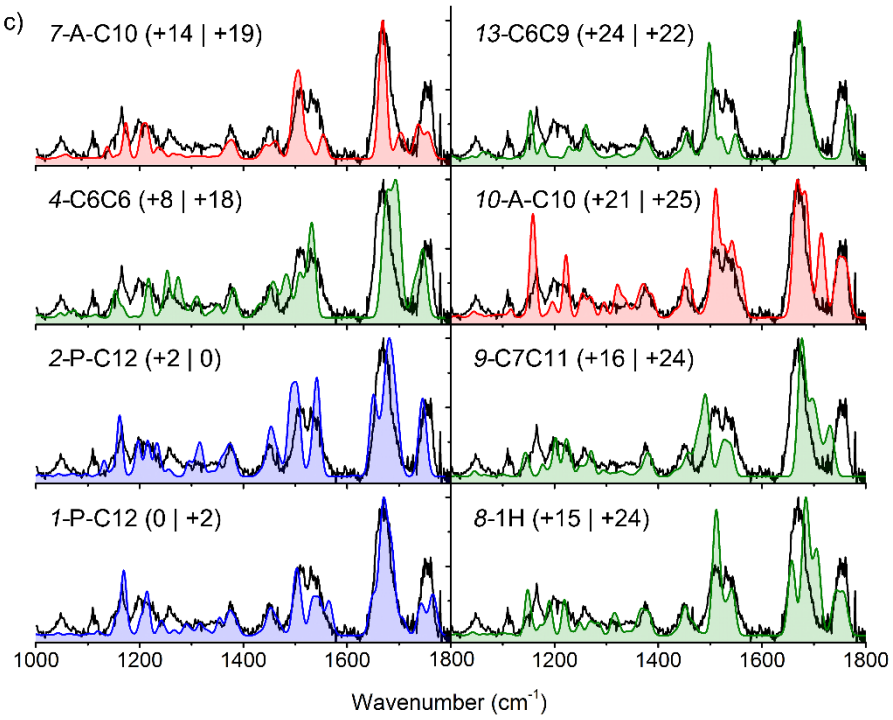
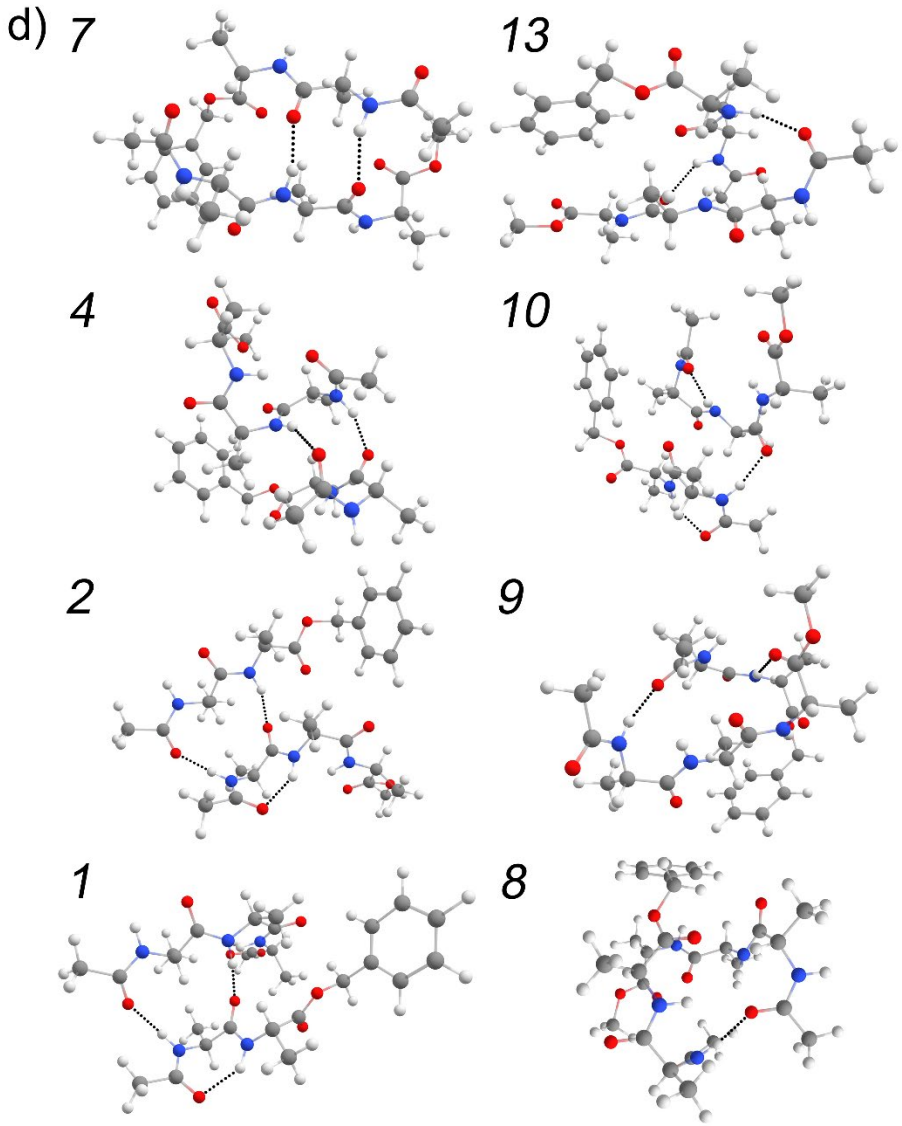


Figure SI.8: a) Relative zero-point corrected energies of all calculated conformers of the dimer of peptide B+3 and their respective hydrogen bonding patterns: green diamant: singly hydrogen bonded dimer, green triangle: other structures with 2 hydrogen bonds, red triangle: anti-parallel C-10, red dot: anti-parallel C-14, blue cube: parallel C-10; b) Three possible hydrogen bond patterns, 1 parallel and 2 anti-parallel.



c) Infrared spectra of the eight lowest energy structures for each family of dimer B3, with between brackets the relative energies in kJ/mol (zero-point corrected energy | With Gibbs free energy at 300K).



d) Structures belonging to spectra of dimer B3 shown in c)