

Supplementary Materials for Article

# Structural Properties of Phenylalanine-Based Dimers Revealed Using IR Action Spectroscopy

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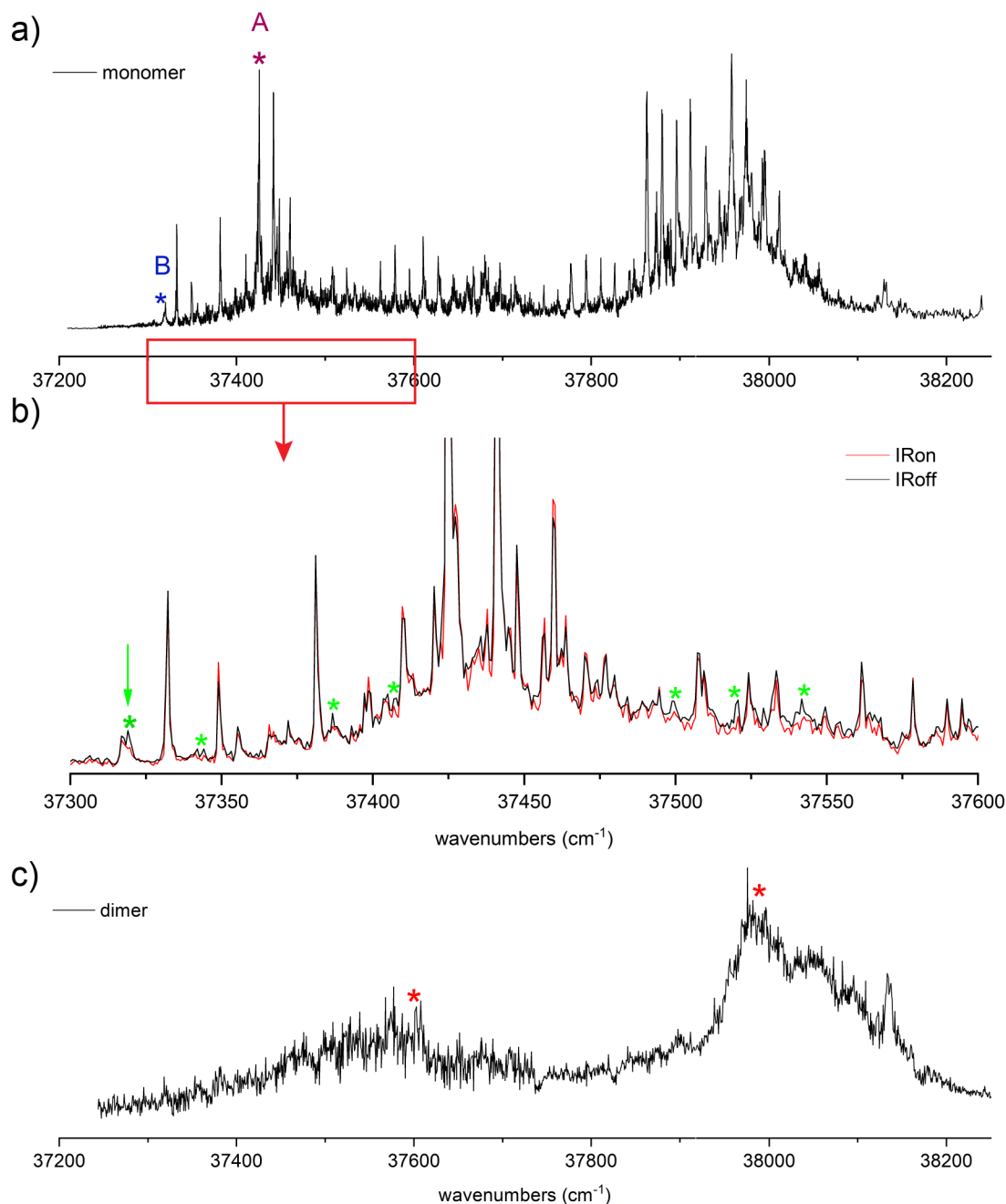
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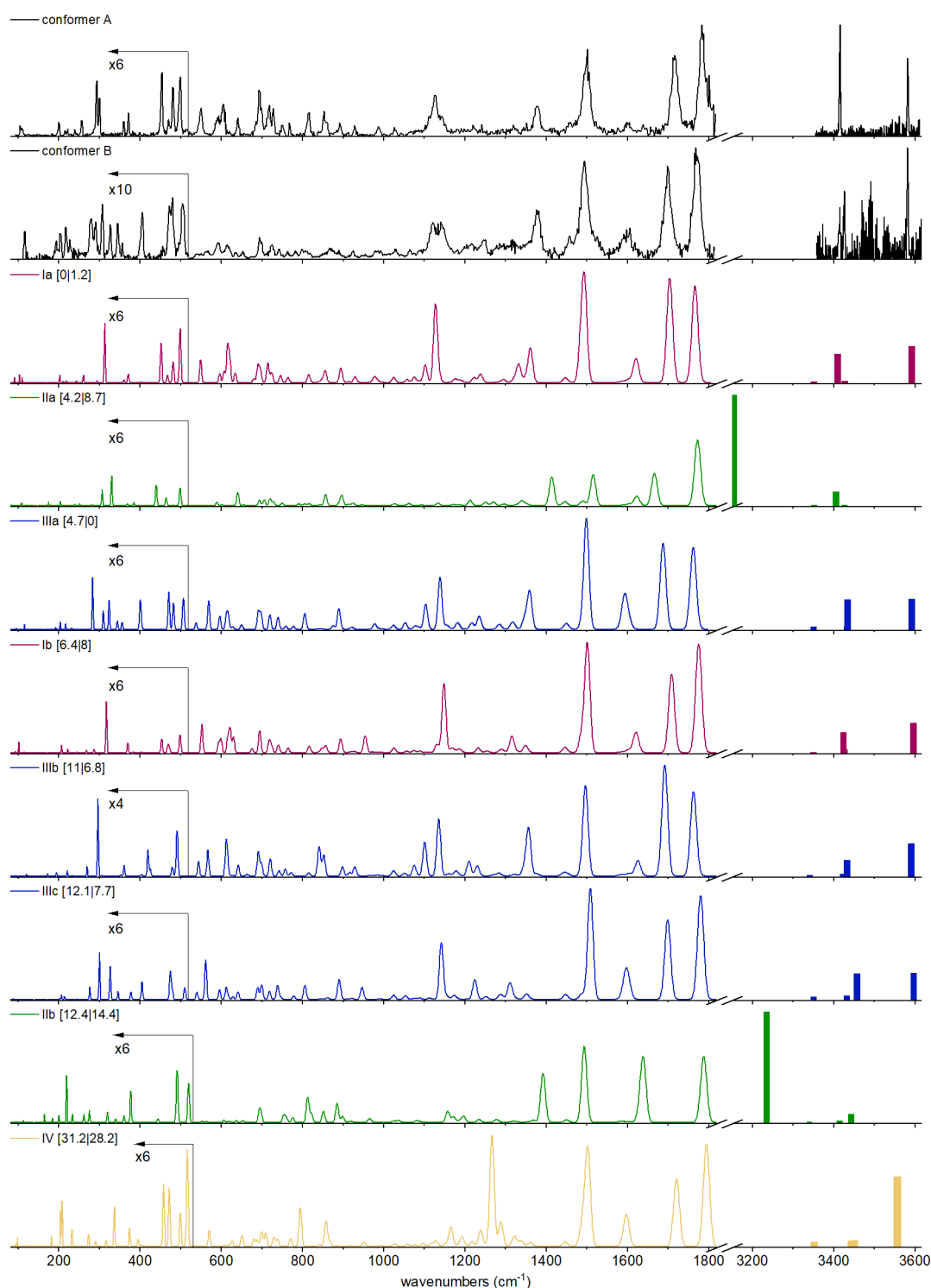
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# 1. REMPI spectra of the PhgPhg monomer and dimer and IR-UV hole-burning spectrum of the PhgPhg monomer



**Figure S1:** REMPI spectra of the PhgPhg monomer and dimer and IR-UV hole-burning spectrum of the PhgPhg monomer: **(a)** REMPI spectrum of the PhgPhg monomer. The IR spectrum of conformer A was recorded at 37426  $\text{cm}^{-1}$  (purple asterisk) and of conformer B at 37319  $\text{cm}^{-1}$  (blue asterisk). **(b)** IR-UV hole-burning spectrum of the PhgPhg monomer between 37300–37600  $\text{cm}^{-1}$  as is indicated by the red box in **(a)**. The IR laser was set at 3426  $\text{cm}^{-1}$  corresponding to the unique vibrational transition of conformer B. The green asterisks indicate the depletion in the UV signal meaning that these transitions correspond to conformer B. The green arrow shows the UV wavenumber that was selected to record the IR spectrum of conformer B. **(c)** REMPI spectrum of the PhgPhg dimer. The IR spectrum of the PhgPhg dimer was obtained at 37603  $\text{cm}^{-1}$  and 37988  $\text{cm}^{-1}$  (red asterisks).

## 2. Theoretical IR spectra of the structural families of the PhgPhg monomer



**Figure S2:** Theoretical IR spectra of the structural families of the PhgPhg monomer. Experimental (black, top) and calculated (colored) IR spectra of the families of PhgPhg monomers, arranged from lowest energy to highest (top to bottom). Calculated spectra are scaled by 0.976 (1800-100  $\text{cm}^{-1}$ ) and 0.956 (3100-3600  $\text{cm}^{-1}$ ), calculations have been done at the B3LYP-D3/6-311+G(d,p) level, their zero-point energies and Gibbs free energies at 300 K in kJ/mol are shown between square brackets. The region below 520  $\text{cm}^{-1}$  was multiplied for clarity (multiplication factor indicated).

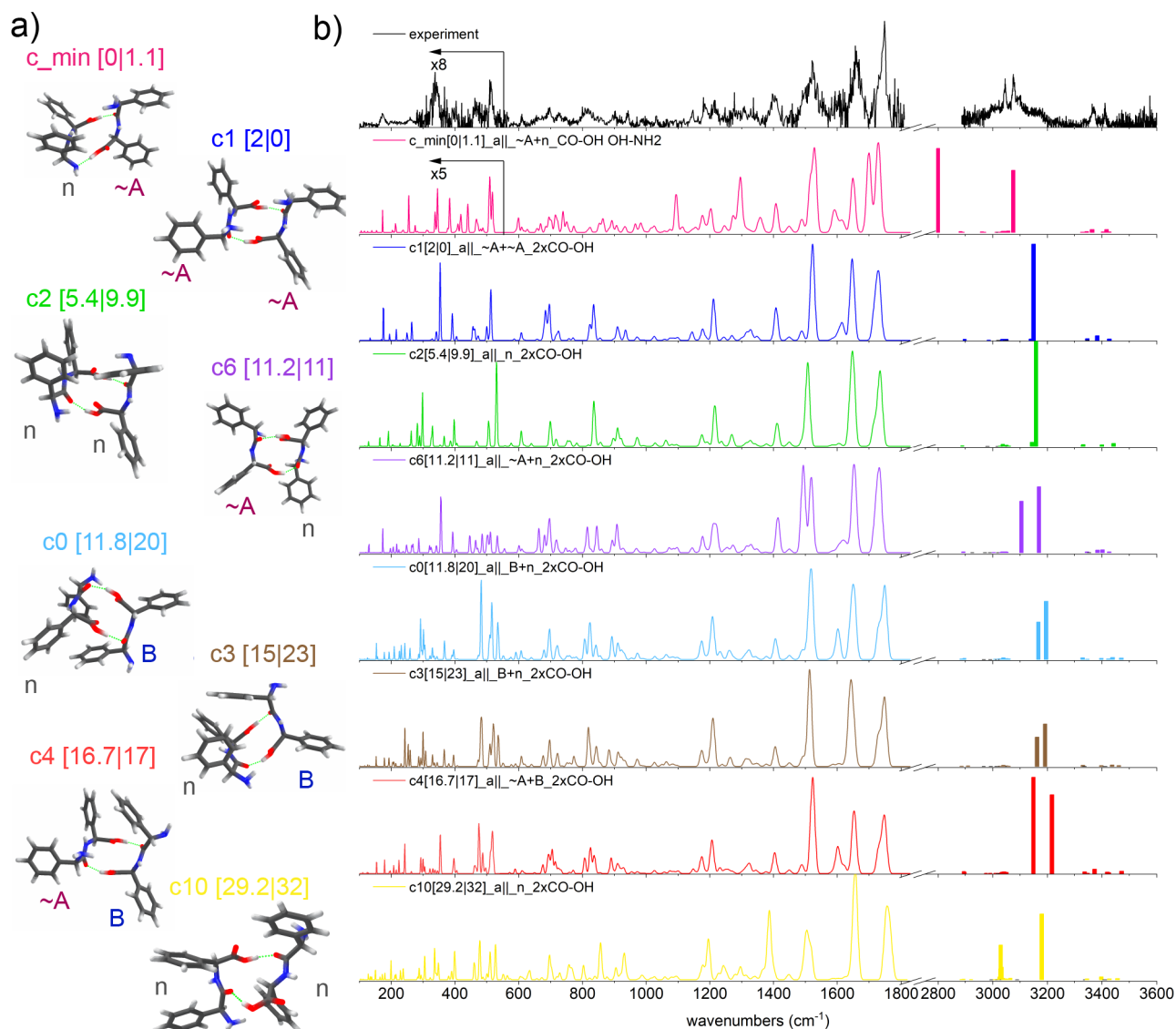
### 3. Theoretical IR frequencies characteristic for the PhgPhg monomer

**Table S1:** Experimentally observed (bold) and calculated frequencies in the amide I and II region for the PhgPhg monomer<sup>1</sup>

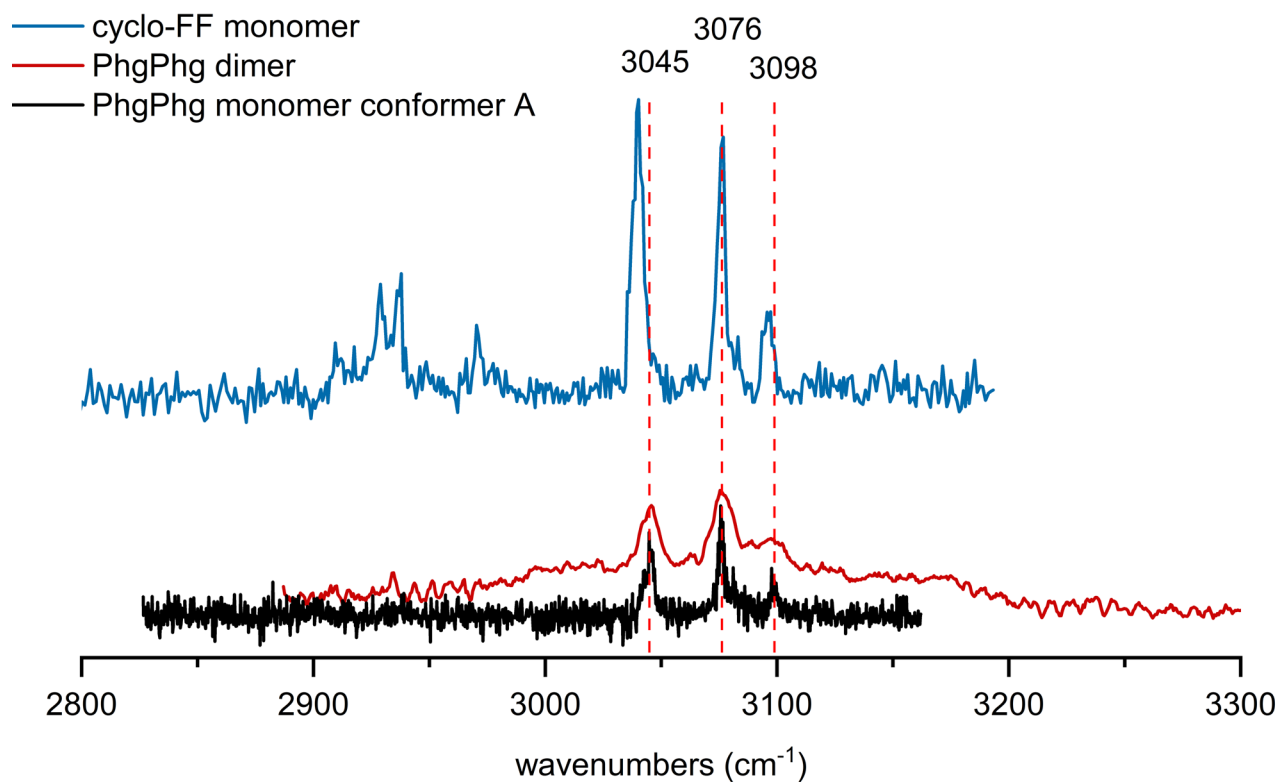
Structure	Carboxylic C=O stretch	Peptide C=O stretch	NH bend	NH <sub>2</sub> scissoring
Ia	1768 C5	1704 free	1493 2XC5	1621 -NH
IIa	1773 free	1669 C7	1515 C5 -NH <sub>2</sub>	1622 -NH
IIIa	1763 C5	1686 C5 -NH <sub>2</sub>	1499 C5 C=O	1596 -CO
Ib	1775 free	1708 free	1502 2XC5 -OH	1620 -NH
IIIb	1763 C5	1690 free	1498 C5 C=O	1625 free
IIIc	1780 free	1698 C5 -NH <sub>2</sub>	1509 C5 -OH	1599 -CO
IIb	1788 free	1639 C5 -NH <sub>2</sub> C7	1493 $\pi$ -interactions	1630 -CO weak
IV	1794 free	1720 C5 -NH <sub>2</sub>	1502 C5 -OH	1597 -CO
<b>Conformer A</b>	<b>1783</b>	<b>1717</b>	<b>1497</b>	<b>1600</b>
<b>Conformer B</b>	<b>1770</b>	<b>1700</b>	<b>1495</b>	<b>1601</b>

<sup>1</sup>Frequencies are given in cm<sup>-1</sup>. Calculated frequencies are scaled by 0.976.

#### 4. Theoretical IR spectra of the antiparallel family of the PhgPhg dimer and their structures



**Figure S3:** Theoretical IR spectra of the antiparallel family of the PhgPhg dimer and their structures: **(a)** Structures of the antiparallel family of the PhgPhg dimer with indications of conformation A, B or none of them (n) of the monomer and their zero-point energies and Gibbs free energies at 300 K in kJ/mol shown between square brackets. Intermolecular hydrogen bonds are shown in green dashed lines. **(b)** Experimental (black, top) and calculated (colored) IR spectra of the lowest energy structure (pink) and structures from the antiparallel 2xCO-OH family of the PhgPhg dimer, arranged from lowest energy to highest (top to bottom). Calculated spectra are scaled by 0.976 (1800-100 cm<sup>-1</sup>) and 0.956 (2900-3600 cm<sup>-1</sup>), calculations have been done at the B3LYP-D3/6-311+G(d,p) level. The region below 570 cm<sup>-1</sup> was multiplied for clarity by 8 for the experimental data and by 5 for all calculated spectra.



**Figure S4:** Comparison of IR spectra in the 3  $\mu\text{m}$  region. IR spectra of the cyclo-FF monomer (dominant conformer, blue), the PhgPhg monomer (conformer A, black) and dimer (red) in the 3  $\mu\text{m}$  region. IR spectrum of cyclo-FF monomer was recorded at the UV wavelength of 37588  $\text{cm}^{-1}$ . The red dashed lines indicate the positions of the peaks that are present in the spectra of all molecules.

## 5. Theoretical IR frequencies characteristic for the PhgPhg dimer

**Table S2:** Experimentally observed (bold) and calculated frequencies in the amide I and II region for the PhgPhg dimer<sup>1</sup>

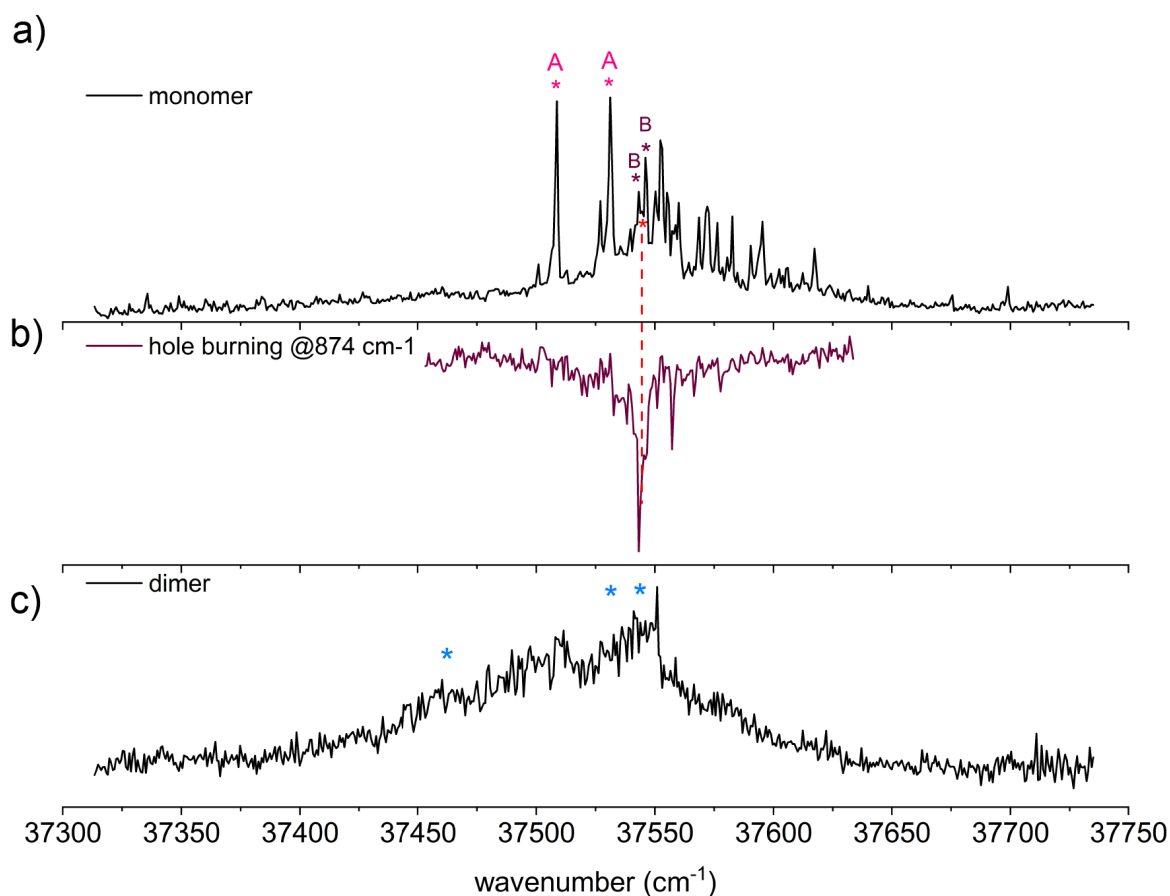
Carboxylic C=O stretch		Peptide C=O stretch		NH bend		NH <sub>2</sub> scissoring	
Free OH is free	1776-1760	Free	1700-1685	Free	1530-1495	Free	1630-1624
Free OH is HB	1766-1720	HB C=O...OH intra	1665-1644			NH <sub>2</sub> – $\pi$ interaction	1645-1620
HB C=O...OH inter	1722 (w) <sup>2</sup> 1693 (s)	HB C=O...OH inter	1653-1630	HB NH...C=O inter	1560-1525	NH <sub>2</sub> ...NH HB intra	1627-1614
HB C=O...NH inter	1747 (w) 1713 (s)	HB C=O...NH inter	1660-1653			NH <sub>2</sub> ...C=O HB intra	1600-1579
						NH <sub>2</sub> ...OH HB inter	1632-1609
Experiment	1748	Experiment	1660	Experiment	Broad, maximum at 1522	Experiment	Broad, max at 1607

<sup>1</sup>Frequencies are given in cm<sup>-1</sup>. Calculated frequencies are scaled by 0.976.

<sup>2</sup>The (w) means weak hydrogen bond, while (s) refers to the group involved in a strong hydrogen bond. Free means no intermolecular hydrogen bonds, though the group can have intramolecular interactions within the monomer unit.

## 6. REMPI spectra of the FF monomer and dimer and IR-UV hole-burning spectrum of the FF monomer

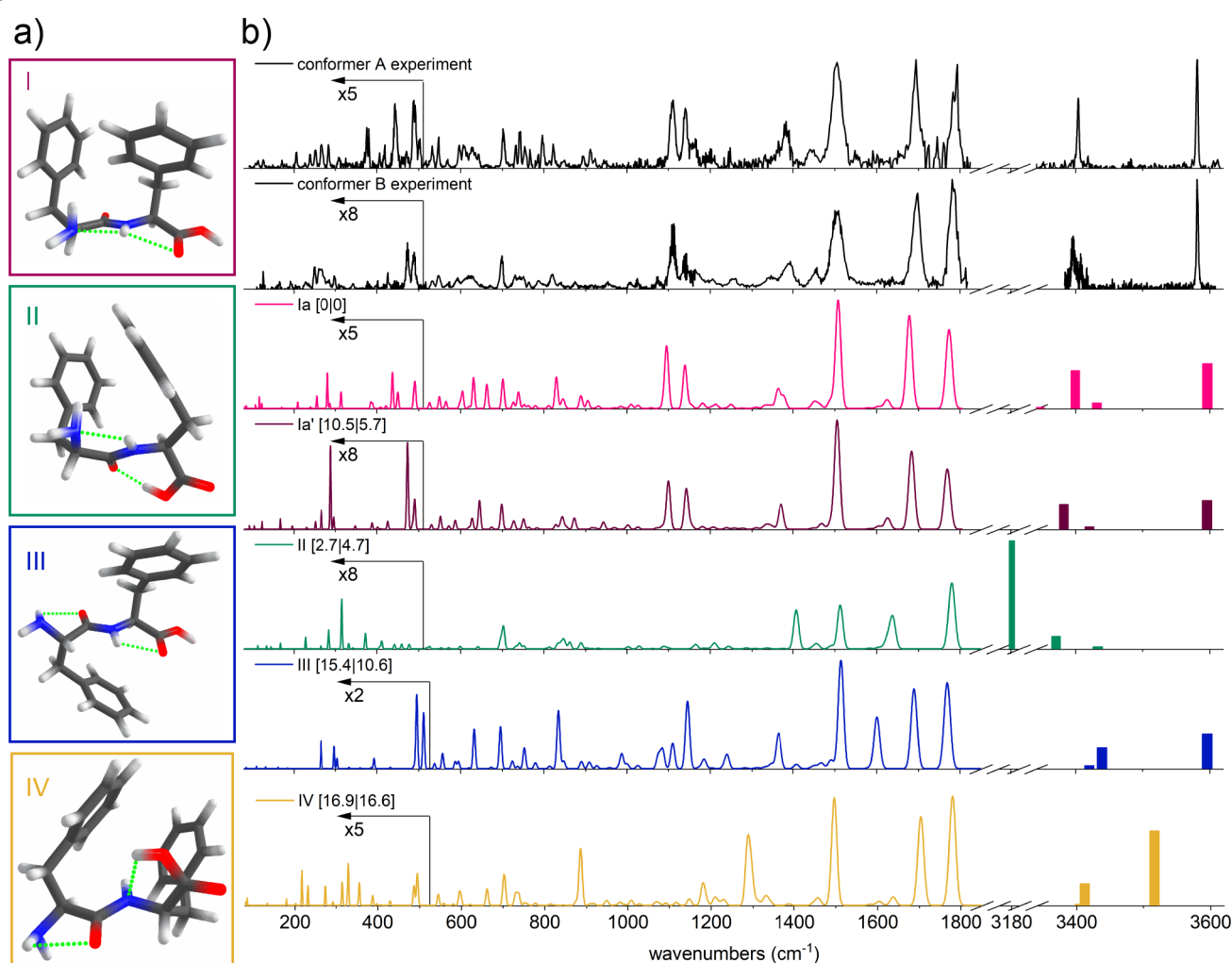
The REMPI spectrum of the FF monomer has already been reported by Abo-Riziq et al. [1] and Pérez-Mellor et al. [2]. The electronic spectrum shown in this paper is similar to those reported earlier, however the positions of the peaks are slightly shifted probably due to different laser calibrations. The presence of two conformations of the monomer was reported in both papers. In this work, the existence of the second conformer (B, marked with purple asterisks) was also confirmed using IR-UV hole-burning spectroscopy (see Figure S5b). The corresponding excitation UV wavenumbers selected for the IR-UV ion dip spectroscopy experiment are marked with the pink (conformer A) and red (conformer B) asterisks in Figure S5a. The IR spectrum of conformer B was recorded in between two peaks corresponding to the UV transitions of two chromophores of conformer B. The REMPI spectrum of the dimer of FF is shown in Figure S5c with the blue asterisks indicating the position of the UV wavenumbers chosen to obtain the IR spectrum. The resulting IR spectra of the dimer are all the same, however considering the broadness of both the UV and IR spectra the presence of multiple conformations for the FF dimer cannot be excluded.



**Figure S5:** REMPI spectra of the monomer (a) and dimer of FF (c), and hole-burning spectrum of the monomer (b). The UV excitation wavenumber to record the IR spectrum of conformation A is marked with the pink asterisks (37508 and 37532  $\text{cm}^{-1}$ ) and for conformer B with the red asterisk (at 37544  $\text{cm}^{-1}$ ). The IR-UV hole-burning spectrum was recorded with the IR laser set at 874  $\text{cm}^{-1}$  corresponding to the unique vibrational transition of the conformer B. The blue asterisks indicate the UV wavelengths that were chosen for recording the IR spectrum of the dimer (37462, 37532, and 37544  $\text{cm}^{-1}$ ).

## 7. The structural families of the FF monomer and their IR spectra

DFT calculations resulted in multiple structures of the FF monomer with different hydrogen bond patterns. Among them, the most stable variants with characteristic hydrogen bonds were summarized into four families (see Figure S6a). The types of the families are similar to the ones that were presented for the PhgPhg monomer. The I family has two hydrogen bonds with the NH group interacting with the carboxylic OH and the N-terminal NH<sub>2</sub> group, while the OH group remains free. The II family is characterized by the OH group hydrogen bonded to the peptide C=O. The III family has two hydrogen bonds between the peptide C=O...NH and the carboxylic C=O...NH<sub>2</sub> with two aromatic rings pointing to different sides of the peptide backbone. The IV family has its OH group hydrogen bonded with NH, and the peptide C=O interacting with NH<sub>2</sub>. The families are listed by their lowest energy structures from lowest (I) in energy to the highest (IV).



**Figure S6:** The structural families of the FF monomer and their IR spectra: (a) The structural families of the FF monomer. (b) The experimental spectrum of the conformers A and B of the monomer (black, top) and the calculated IR spectra of the assigned structures (pink and purple); and the theoretical spectra of the rest of the families, arranged from lowest energy to highest (top to bottom) with their zero-point energies and Gibbs free energies at 300 K in kJ/mol shown between square brackets. Calculated spectra are scaled by 0.976 (1800–100 cm<sup>-1</sup>) and 0.956 (2900–3600 cm<sup>-1</sup>), calculations have been done at the B3LYP-D3/6-311+G(d,p) level. The region below 520 cm<sup>-1</sup> was multiplied for clarity with multiplication factors indicated.

The experimental IR spectra of both conformations of the FF monomer are shown in Figure S6b (top, black). The amide A region has been reported previously by Abo-Riziq et al. [1] and Pérez-Mellor et al. [2]. Here, we will describe the IR pattern in the 3 μm region, as well as in the mid and far-IR region between 1800 and 100 cm<sup>-1</sup> which extends the analysis. Additionally, the differences and similarities of the structural assignments will be discussed. Conformation A has three peaks at 3404, 3418 and 3581 cm<sup>-1</sup>. All frequencies are slightly blueshifted in about 10 cm<sup>-1</sup> compared to the

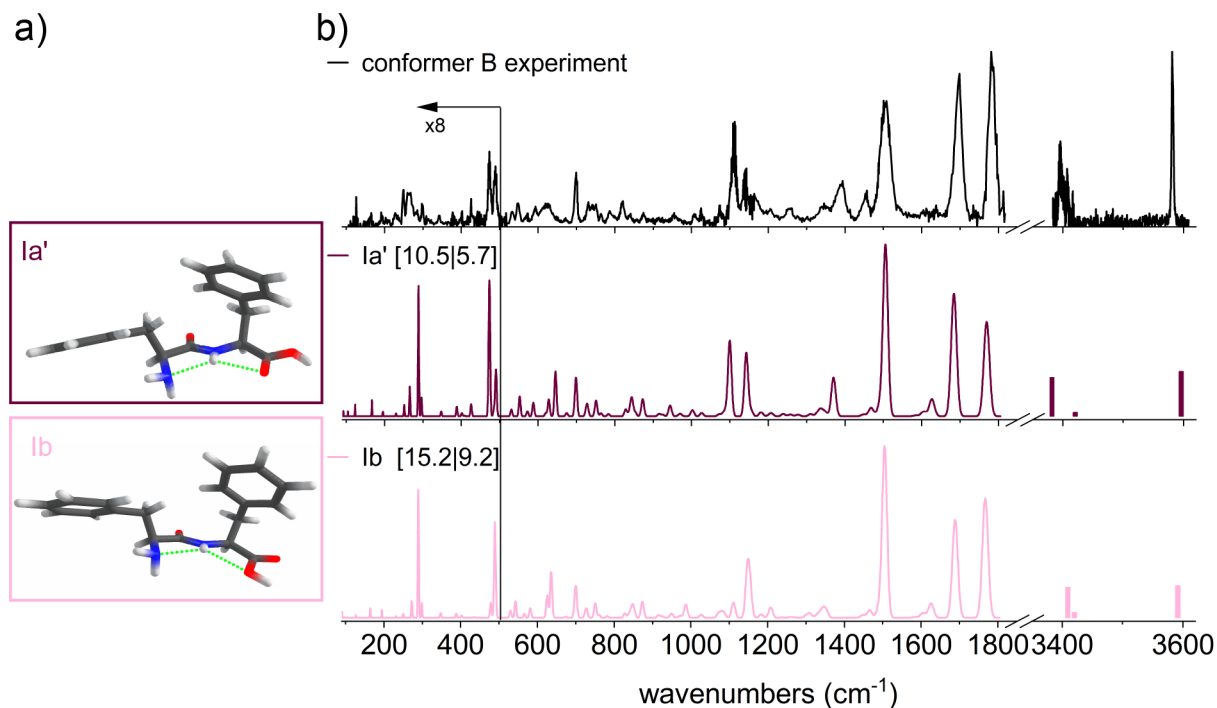
ones reported previously, probably due to the laser calibration, however the pattern remains similar. The first peak at  $3404\text{ cm}^{-1}$  can be assigned to the weakly hydrogen bonded NH group, while the second weak transition at  $3418\text{ cm}^{-1}$  originates from an  $\text{NH}_2$  asymmetric stretch, and the third peak at  $3581\text{ cm}^{-1}$  belongs to a free OH stretch. The experimental spectrum of conformer B has four transitions in the amide A region and the peaks are slightly broader. The first peak at  $3396\text{ cm}^{-1}$  corresponds to the weakly hydrogen bonded NH group, the second small peak at  $3408\text{ cm}^{-1}$  originates from the  $\text{NH}_2$  asymmetric stretch, while the third peak at  $3416\text{ cm}^{-1}$  hasn't been reported earlier. This vibration possibly belongs to a combination band or an overtone. The last peak at  $3582\text{ cm}^{-1}$  is a typical peak of the free OH stretching vibration. The position of this OH band around  $3580\text{ cm}^{-1}$  for both conformers allows us to exclude the OH hydrogen bonded structures from the II and IV families. The III family that is characterized by the free OH group predicts the OH vibration well, however in the NH region around  $3400\text{ cm}^{-1}$  the position of the peaks does not match with the experimental values. The  $\text{NH}_2$  asymmetric stretch is more red shifted and has a lower energy than the NH stretching mode. Therefore, the III family can be also excluded and therefore both conformers should belong to the I structural family. The mid- and far-IR regions can confirm this and provide a more detailed structural assignment.

The experimental spectra of the conformations A and B are very similar in the  $1800\text{--}1000\text{ cm}^{-1}$  region. The carboxylic  $\text{C}=\text{O}$  stretch vibration is located at around  $1780\text{ cm}^{-1}$  for both conformers and suggests that the  $\text{C}=\text{O}$  can be involved in a weak C5 interaction. The peptide  $\text{C}=\text{O}$  peak is present at  $1695\text{ cm}^{-1}$ , which is typical for a free  $\text{C}=\text{O}$  group. The peak at  $1504\text{ cm}^{-1}$  is assigned for both conformers to the NH group that is involved in a weak C5 or  $\text{NH}\text{--}\pi$  interaction. Therefore, that region confirms that both conformers originate from the I structural family. The far-IR region below  $1000\text{ cm}^{-1}$  gives more insight into the structural assignment, since it is sensitive to small alterations in the orientation of the functional groups and comprises global motions of the whole molecule. The two conformers are also more different in that region, especially below  $500\text{ cm}^{-1}$ . The IR spectrum of conformer A has a broad peak around  $480\text{ cm}^{-1}$ , followed by another quite broad peak at  $444\text{ cm}^{-1}$ , a doublet at  $412\text{ cm}^{-1}$ , another broad feature at  $376\text{ cm}^{-1}$ , a quartet of peaks between  $300\text{--}226\text{ cm}^{-1}$ , and a number of smaller peaks below  $200\text{ cm}^{-1}$ . Conformer B has a completely different IR pattern in this region, such as a doublet at  $478\text{ cm}^{-1}$ , followed by a number of low intensity peaks, and relatively strong transitions around  $260\text{ cm}^{-1}$ . Based on the comparison of the pattern of IR transitions in the far-IR region, we can assign conformations A and B to their structures (pink and purple spectra respectively in Figure S6b). The conformer A is assigned to the most stable structure Ia, while the assigned structure of conformer B (Ia') is more extended due to the aromatic rings rotated away from each other and is therefore  $10.5\text{ kJ/mol}$  higher in energy.

The structural assignments that were reported previously by Abo-Riziq et al. [1] are exactly similar to our results, however our structures are assigned vice versa. Since they did not observed low intensity peak at  $3418\text{ cm}^{-1}$  both in experiment for conformer A and in calculations for the Ia' structure, they assigned the more extended structure to conformer A, and the more compact Ia to conformer B, while our results show it the other way around. This can originate from experimental limitations in sensitivity and/or calculations with lower basis sets and functional without empirical dispersion (B3LYP/6-311G(d,p)). In our work, the B3LYP-D3/6-311+G(d,p) functional and basis set were used. Additionally, Abo-Riziq et al. reported the structure from the II family with the hydrogen bonded OH group as the most stable one, however, that is different from our findings where the lowest energy structure originates from the I family. That difference could be explained, as was already mentioned in the work of Pérez-Mellor et al. [2], due to the fact that they did not use empirical dispersion in the calculations and consequently aromatic interactions between rings were not taken into account.

The structural assignment made by Pérez-Mellor et al. [2] coincides well with our results. They used the same dispersion-corrected functional B3LYP-D3 with an even higher 6-311++g(d,p) basis set, which includes diffuse functions also for hydrogen. Conformer A is assigned to the most stable structure which is exactly the same as our assignment. Conformer B is assigned to the more extended structure which is very similar to our assignment, except for the rotated COOH group by  $180^\circ$ . Figure S7 shows the comparison between the experimental IR spectrum of conformer B and the two structures Ia' and Ib which differ only in the orientation of the COOH group and are calculated at the level of theory that we used in the current work. Two theoretical spectra are different in the amide A region, where the predicted frequency of the NH stretch is shifted from the experimental value to the red in the Ia' structure and to the blue in the Ib structure. However, the spacing between two peaks of about 10 wavenumbers corresponding to NH and  $\text{NH}_2$  stretch vibrations is predicted better in Ib structure. Based on the spectra only in the  $3\text{ }\mu\text{m}$  region, Ib looks like a possible assignment for conformer B, however mid- and far-IR regions help us to make a more precise assignment. In the amide I and II region both spectra are equal, however Ia' predicts the doublet at about  $1400\text{ cm}^{-1}$  better, as well as another doublet at  $1100\text{ cm}^{-1}$  in terms of ratio of the two peaks. Only a small peak at  $1073\text{ cm}^{-1}$  is predicted better by Ib than by Ia'. The doublet around  $1020\text{ cm}^{-1}$  is also described better by structure Ia', along with another small peak at  $950\text{ cm}^{-1}$ .

Below  $950\text{ cm}^{-1}$  the two calculated structures become almost the same, except for the doublet at  $485\text{ cm}^{-1}$ , which again Ia' describes better than Ib in terms of relative intensities. Therefore, based on the comparison of experimental and theoretical spectra in the mid- and far-IR region, we confidently assign conformer B to the Ia' structure, which also is lower in energy than Ib.



**Figure S7:** Comparison with previous assignment for conformer B of the FF monomer: (a) The calculated structures Ia' and Ib. (b) The experimental spectrum of conformer B of the monomer (black, top) and the calculated IR spectra of the two structures (purple and pink) with their zero-point energies and Gibbs free energies at 300 K in kJ/mol shown between square brackets. Calculated spectra are scaled by 0.976 ( $1800\text{--}100\text{ cm}^{-1}$ ) and 0.956 ( $3300\text{--}3600\text{ cm}^{-1}$ ), calculations have been done at the B3LYP-D3/6-311+G(d,p) level. The region below  $520\text{ cm}^{-1}$  was multiplied for clarity by 8 for all spectra.

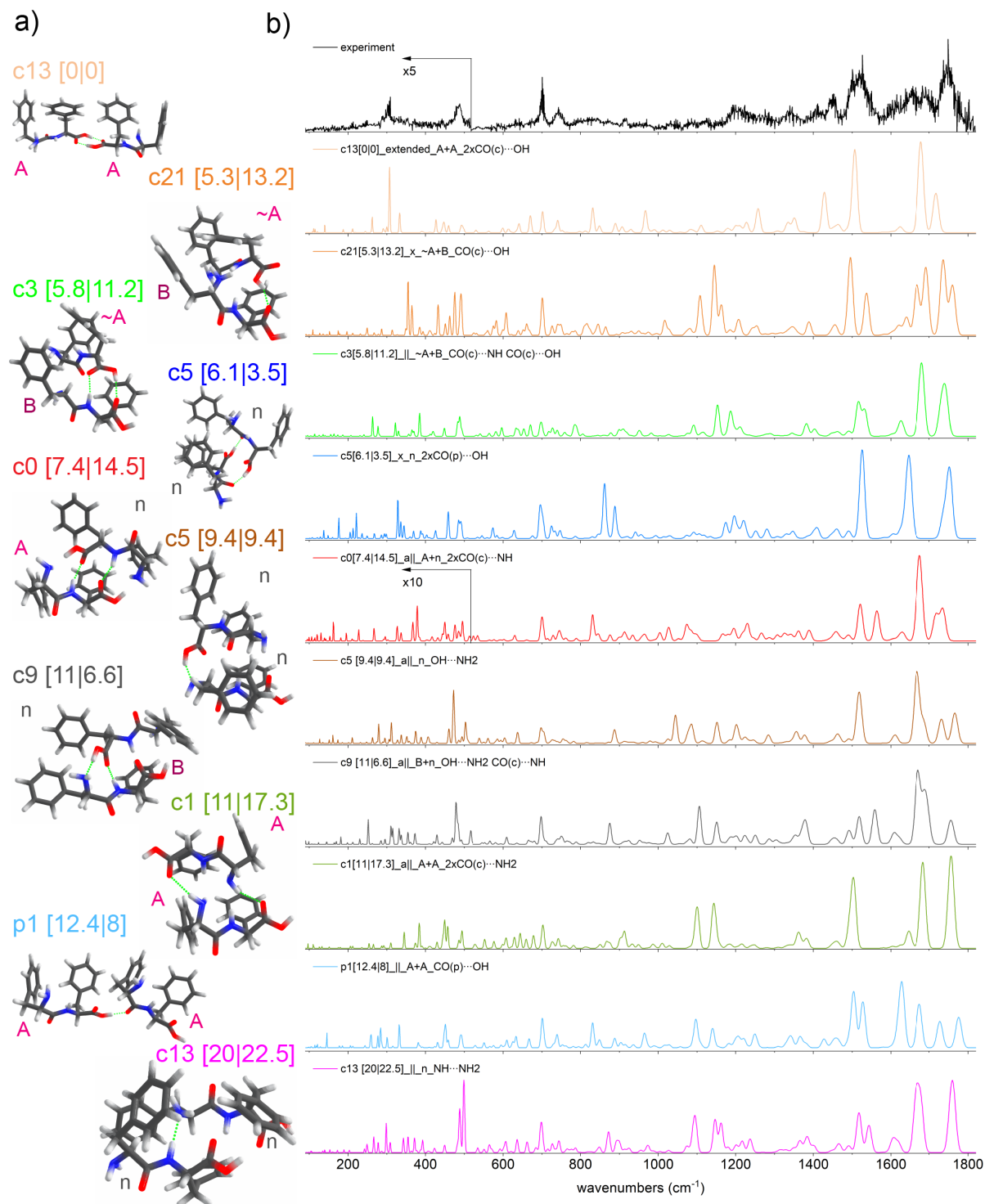
## 8. Theoretical IR frequencies characteristic for the FF dimer

**Table S3:** Experimentally observed (bold) and calculated frequencies in the amide I and II region for the FF dimer<sup>1</sup>

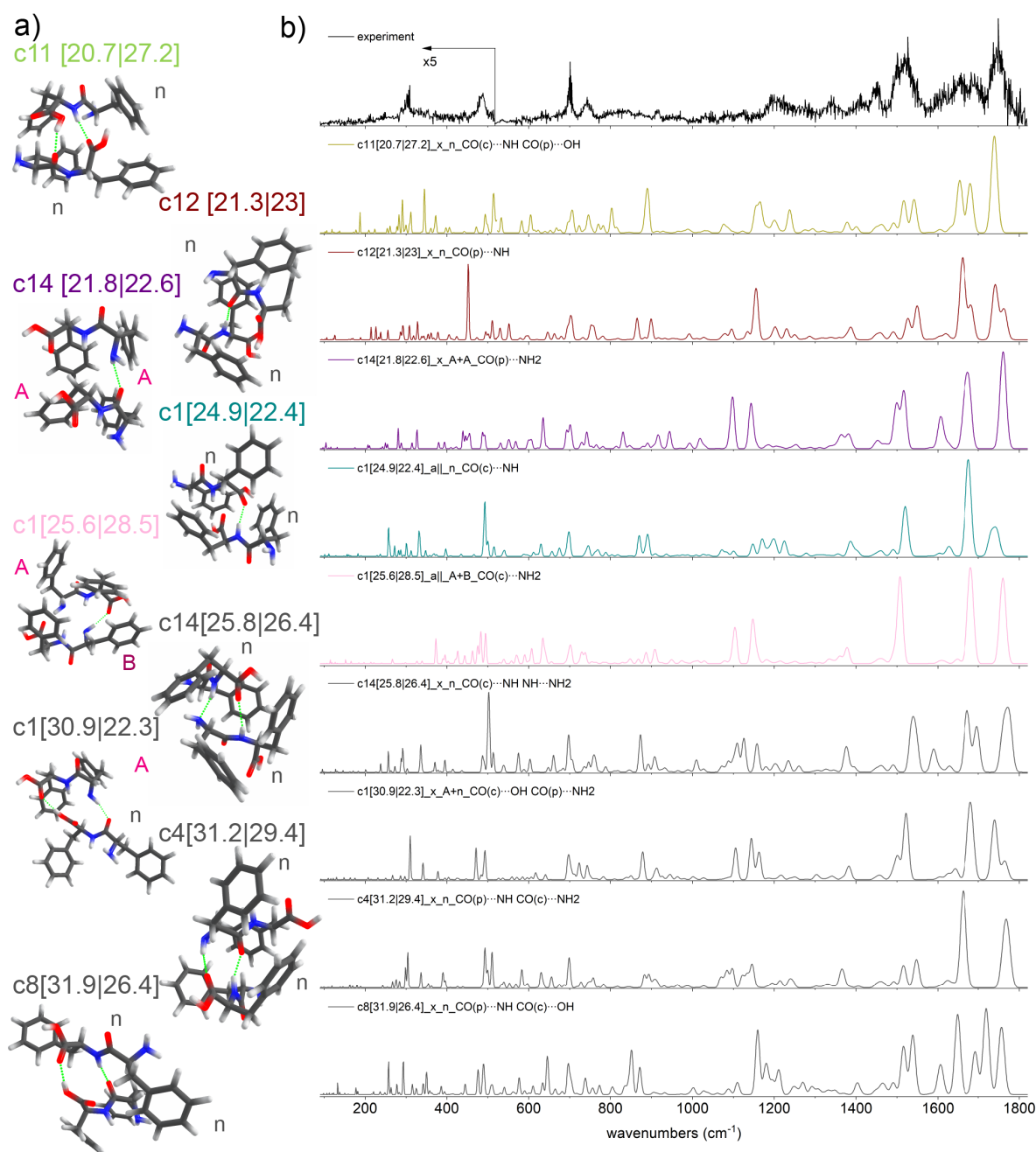
Carboxylic C=O stretch		Peptide C=O stretch		NH bend		NH <sub>2</sub> scissoring	
Free OH is free	1770-1740	Free	1693-1670	Free	1527-1507	Free	1635-1626
Free OH is HB	1755-1710						
		HB CO...NH <sub>2</sub>	1669-1662	HB NH...NH <sub>2</sub>	1573-1543	NH <sub>2</sub> ...CO intra/inter	1605/1648-1606
HB C=O...OH inter	1743-1720	HB C=O...OH inter	1653-1630	HB NH...C=O inter	1550-1530	NH <sub>2</sub> ...NH intra/inter	1625/1658-1607
HB C=O...NH inter	1752-1695	HB C=O...NH inter	1675-1650			NH <sub>2</sub> ...OH inter	1611-1603
<b>Experiment</b>	<b>1747</b>	<b>Experiment</b>	<b>1691 1654</b>	<b>Experiment</b>	<b>Broad, max at 1522</b>	<b>Experiment</b>	<b>Broad, max at 1614</b>

<sup>1</sup>Frequencies are given in cm<sup>-1</sup>. Calculated frequencies are scaled by 0.976.

## 9. Theoretical IR spectra of the structural families of the FF dimer

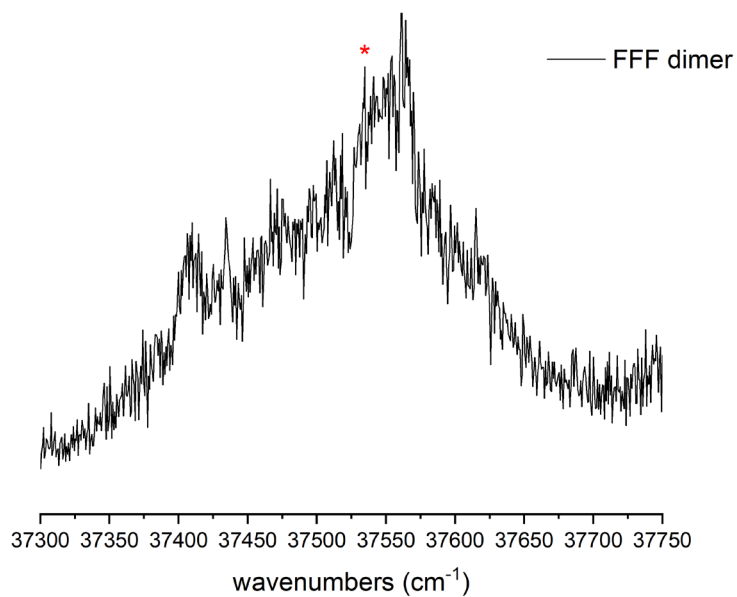


**Figure S8.1:** Theoretical IR spectra of the structural families of the FF dimer: **(a)** The structures of the FF dimer with an indication of the monomeric backbones originating from conformation A, B or none of them (n) and their zero-point energies and Gibbs free energies at 300 K in kJ/mol shown between square brackets. Intermolecular hydrogen bonds are shown in green dashed lines. **(b)** Experimental (black, top) and calculated (colored) IR spectra of the structures, arranged from lowest energy to highest (top to bottom). The types of intermolecular hydrogen bonds are named in the legend, as well as parallel (||), antiparallel (a||) or random (x) orientation of monomers with respect to each other. Calculated spectra are scaled by 0.976 (1800–100  $\text{cm}^{-1}$ ), calculations have been done at the B3LYP-D3/6-311+G(d,p) level. The region below 520  $\text{cm}^{-1}$  was multiplied for clarity by 5 for all spectra and by 10 for c0 spectra (red).



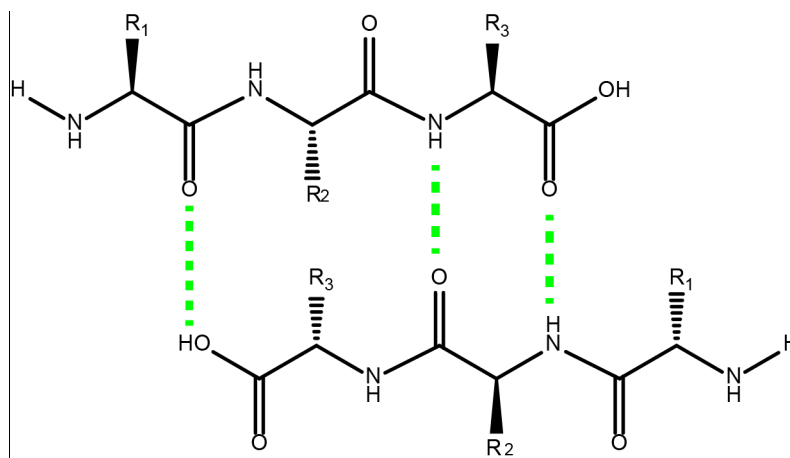
**Figure S8.2:** Theoretical IR spectra of the structural families of the FF dimer: **(a)** The structures of the FF dimer with an indication of the monomeric backbones originating from conformation A, B or none of them (n) and their zero-point energies and Gibbs free energies at 300 K in kJ/mol shown between square brackets. Intermolecular hydrogen bonds are shown in green dashed lines. **(b)** Experimental (black, top) and calculated (colored) IR spectra of the structures, arranged from lowest energy to highest (top to bottom). The types of intermolecular hydrogen bonds are named in the legend, as well as parallel (||), antiparallel (a||) or random (x) orientation of monomers with respect to each other. Calculated spectra are scaled by 0.976 (1800–100  $\text{cm}^{-1}$ ), calculations have been done at the B3LYP-D3/6-311+G(d,p) level. The region below 520  $\text{cm}^{-1}$  was multiplied for clarity by 5.

## 10. REMPI spectrum of the FFF dimer



**Figure S9:** REMPI spectrum of the FFF dimer. The red asterisk indicates the position of UV excitation wavelength ( $37535 \text{ cm}^{-1}$ ) that was chosen to record the IR spectrum.

## 11. Possible structure of the FFF dimer



**Figure S10:** Possible structure of the FFF dimer. Intermolecular hydrogen bonds are shown in green dashed lines.

## 12. XYZ files of assigned structures

### PhgPhg monomer, conformer A

#P B3LYP/6-311+G\*\* EmpiricalDispersion=GD3 Guess=Always freq=noraman Opt=tight int=ultrafine

N	-1.855159000	-2.900538000	0.167648000
H	-2.785973000	-3.087721000	0.526005000
H	-1.518079000	-3.749152000	-0.274490000
C	-1.881617000	-1.791782000	-0.789998000
C	-3.472724000	1.658359000	-0.523135000
C	-2.961087000	0.472624000	-1.042178000
C	-2.520137000	-0.544390000	-0.189014000
C	-2.598965000	-0.352786000	1.193548000
C	-3.117469000	0.833774000	1.712806000
C	-3.553363000	1.843206000	0.857391000
H	-3.804956000	2.440243000	-1.196710000
H	-2.876642000	0.339446000	-2.114796000
H	-2.241334000	-1.124647000	1.864213000
H	-3.173692000	0.968953000	2.787338000
H	-3.953085000	2.766451000	1.261592000
H	-2.394103000	-2.028941000	-1.729408000
C	-0.450208000	-1.385555000	-1.201981000
O	-0.212841000	-0.912216000	-2.300886000
N	0.475645000	-1.526852000	-0.220293000
H	0.189630000	-1.931402000	0.663368000
C	1.788680000	-0.932549000	-0.335122000
C	0.805214000	2.639348000	0.633047000
C	0.793327000	1.250323000	0.520522000
C	1.787504000	0.596730000	-0.207853000
C	2.796711000	1.344358000	-0.817546000
C	2.811583000	2.731776000	-0.700180000
C	1.814737000	3.383515000	0.026160000
H	0.017959000	3.135608000	1.189118000
H	-0.007034000	0.683671000	0.979210000
H	3.568573000	0.840175000	-1.388404000
H	3.594871000	3.304309000	-1.184186000
H	1.821307000	4.464443000	0.110185000
H	2.217459000	-1.193281000	-1.305424000
C	2.670355000	-1.521270000	0.759895000
O	3.978206000	-1.348546000	0.483741000
H	4.486147000	-1.678319000	1.240445000
O	2.264673000	-2.053260000	1.762431000

### PhgPhg monomer, conformer B

#p B3LYP/6-311+G\*\* freq=noraman Opt=tight EmpiricalDispersion=GD3

N	-2.435030000	-2.782633000	0.826968000
H	-3.128436000	-3.313932000	0.312891000
H	-1.742018000	-3.423195000	1.202375000
C	-1.773674000	-1.815504000	-0.046758000
C	-4.289293000	1.032260000	0.307226000
C	-3.510057000	-0.083789000	0.599613000
C	-2.675521000	-0.639608000	-0.376556000
C	-2.644859000	-0.061953000	-1.649603000
C	-3.423666000	1.057607000	-1.942902000
C	-4.246946000	1.608283000	-0.963346000
H	-4.930633000	1.455610000	1.072312000
H	-3.542733000	-0.543500000	1.579865000
H	-2.006414000	-0.490549000	-2.416292000
H	-3.390025000	1.493933000	-2.934913000
H	-4.853931000	2.478011000	-1.188010000
H	-1.440755000	-2.258715000	-1.001321000
C	-0.441359000	-1.420529000	0.634381000
O	0.235080000	-2.262663000	1.208529000
N	-0.053665000	-0.128314000	0.506878000
H	-0.671257000	0.559214000	0.096899000
C	1.229941000	0.319433000	1.015561000
C	3.403935000	0.349001000	-2.122362000
C	2.367794000	0.610440000	-1.230248000
C	2.378845000	0.043126000	0.047261000
C	3.431404000	-0.790382000	0.421141000

C	4.469247000	-1.052863000	-0.472301000
C	4.458314000	-0.483147000	-1.743825000
H	3.390094000	0.793929000	-3.110987000
H	1.546908000	1.255591000	-1.525925000
H	3.429389000	-1.247554000	1.403983000
H	5.280826000	-1.708002000	-0.176633000
H	5.264547000	-0.688714000	-2.438882000
H	1.433115000	-0.196853000	1.955506000
C	1.143098000	1.814340000	1.288188000
O	2.121898000	2.219682000	2.118284000
H	2.054735000	3.182432000	2.208691000
O	0.326051000	2.556561000	0.802025000

## PhgPhg dimer

#p B3LYP/6-311+G\*\* freq=noraman Opt=tight EmpiricalDispersion=GD3

N	2.346964000	1.203792000	2.149564000
H	2.657343000	1.671158000	2.994393000
H	1.335832000	1.284767000	2.087421000
C	2.949727000	1.828224000	0.967031000
C	6.473466000	3.232745000	0.593204000
C	5.091728000	3.080022000	0.500193000
C	4.453648000	1.999748000	1.115879000
C	5.222120000	1.069328000	1.822981000
C	6.603326000	1.225390000	1.921107000
C	7.233362000	2.306415000	1.306028000
H	6.955338000	4.075946000	0.1111107000
H	4.503070000	3.798205000	-0.059892000
H	4.736341000	0.223674000	2.294727000
H	7.188098000	0.498955000	2.474492000
H	8.308276000	2.426060000	1.381671000
H	2.507712000	2.798866000	0.719804000
C	2.670958000	0.961644000	-0.272700000
O	2.590998000	1.468955000	-1.396787000
N	2.550046000	-0.352928000	-0.025189000
H	2.488545000	-0.606971000	0.955453000
C	2.130710000	-1.317449000	-1.031208000
C	3.598272000	-4.610196000	0.225133000
C	2.813317000	-3.462988000	0.138909000
C	2.949528000	-2.595827000	-0.950051000
C	3.874131000	-2.895575000	-1.951971000
C	4.657110000	-4.045575000	-1.867165000
C	4.521831000	-4.904199000	-0.777852000
H	3.485383000	-5.277345000	1.072307000
H	2.084370000	-3.244554000	0.911634000
H	3.984298000	-2.225878000	-2.797920000
H	5.371768000	-4.269217000	-2.651101000
H	5.130509000	-5.798861000	-0.711473000
H	2.267140000	-0.850380000	-2.004878000
C	0.637104000	-1.614894000	-0.844780000
O	0.009911000	-1.782979000	-1.999572000
H	-0.968852000	-1.852348000	-1.846708000
O	0.113958000	-1.679701000	0.250101000
N	-2.346973000	-1.203790000	2.149563000
H	-1.335840000	-1.284765000	2.087425000
H	-2.657356000	-1.671154000	2.994392000
C	-2.949730000	-1.828224000	0.967028000
C	-6.473461000	-3.232765000	0.593203000
C	-5.091724000	-3.080035000	0.500193000
C	-4.453651000	-1.999755000	1.115874000
C	-5.222129000	-1.069334000	1.822970000
C	-6.603333000	-1.225402000	1.921094000
C	-7.233364000	-2.306434000	1.306021000
H	-6.955328000	-4.075971000	0.111111000
H	-4.503062000	-3.798218000	-0.059887000
H	-4.736355000	-0.223675000	2.294712000
H	-7.188110000	-0.498968000	2.474475000
H	-8.308277000	-2.426084000	1.381664000
H	-2.507710000	-2.798863000	0.719801000
C	-2.670963000	-0.961641000	-0.272701000
O	-2.591001000	-1.468951000	-1.396789000
N	-2.550054000	0.352932000	-0.025190000

H	-2.488553000	0.606973000	0.955453000
C	-2.130714000	1.317452000	-1.031207000
C	-4.657093000	4.045599000	-1.867162000
C	-3.874121000	2.895594000	-1.951971000
C	-2.949526000	2.595834000	-0.950047000
C	-2.813315000	3.462988000	0.138919000
C	-3.598264000	4.610200000	0.225145000
C	-4.521815000	4.904216000	-0.777844000
H	-5.371745000	4.269250000	-2.651102000
H	-3.984288000	2.225903000	-2.797925000
H	-2.084374000	3.244545000	0.911647000
H	-3.485374000	5.277344000	1.072323000
H	-5.130487000	5.798881000	-0.711463000
H	-2.267146000	0.850386000	-2.004878000
C	-0.637107000	1.614891000	-0.844779000
O	-0.009915000	1.782981000	-1.999572000
H	0.968848000	1.852348000	-1.846707000
O	-0.113959000	1.679690000	0.250101000

## FF monomer, conformer A

# B3LYP/6-311+G\*\* EmpiricalDispersion=GD3 freq=noraman Opt=tight Guess =Always

N	-0.910473000	-1.362063000	2.207404000
H	-1.370145000	-1.641190000	3.065795000
H	-1.152903000	-0.393086000	2.021567000
C	-1.288163000	-2.229397000	1.090379000
H	-1.213467000	-3.263193000	1.446218000
C	-0.259015000	-2.127967000	-0.053355000
O	-0.502638000	-2.549727000	-1.179080000
C	-2.727212000	-2.037066000	0.536991000
H	-2.884693000	-2.776727000	-0.249693000
H	-3.424196000	-2.260813000	1.350511000
C	-2.990514000	-0.648789000	0.002159000
C	-3.417838000	0.379782000	0.851412000
H	-3.614714000	0.161870000	1.896510000
C	-2.781270000	-0.349439000	-1.351215000
H	-2.436637000	-1.133926000	-2.013978000
C	-3.615275000	1.674422000	0.370512000
H	-3.946984000	2.455826000	1.045603000
C	-2.986922000	0.940505000	-1.835482000
H	-2.818362000	1.152877000	-2.885422000
C	-3.397681000	1.959383000	-0.975707000
H	-3.548853000	2.964487000	-1.352476000
N	0.915793000	-1.558240000	0.292829000
H	1.024642000	-1.243089000	1.249951000
C	1.949123000	-1.289321000	-0.678174000
H	1.991701000	-2.122805000	-1.385211000
C	3.286693000	-1.210818000	0.035354000
O	3.450687000	-1.230708000	1.227693000
C	1.656719000	0.003998000	-1.500616000
H	2.457934000	0.132404000	-2.231478000
H	0.732295000	-0.191193000	-2.047484000
C	1.512374000	1.232106000	-0.634336000
C	0.263999000	1.593424000	-0.115131000
H	-0.614624000	1.020808000	-0.384983000
C	2.627781000	2.005715000	-0.293185000
H	3.601094000	1.744042000	-0.695901000
C	0.134531000	2.695282000	0.727884000
H	-0.845062000	2.961242000	1.108890000
C	2.502235000	3.106703000	0.551707000
H	3.377319000	3.695345000	0.804098000
C	1.254129000	3.453336000	1.067670000
H	1.154837000	4.311637000	1.722750000
O	4.305053000	-1.095282000	-0.849726000
H	5.126589000	-1.037806000	-0.339179000

## FF monomer, conformer B

#p B3LYP/6-311+G\*\* freq=noraman Opt=tight EmpiricalDispersion=GD3

N	-1.278615000	-1.456122000	1.377246000
H	-2.132520000	-1.065295000	1.761624000
H	-1.182194000	-2.396010000	1.746984000

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C	-1.321709000	-1.463350000	-0.087119000
H	-1.942941000	-2.267049000	-0.503334000
C	0.073667000	-1.671407000	-0.693093000
O	0.212143000	-2.018306000	-1.860920000
C	-1.870585000	-0.115587000	-0.612177000
H	-1.232226000	0.686471000	-0.232126000
H	-1.781097000	-0.127387000	-1.701181000
C	-3.305321000	0.123701000	-0.205975000
C	-3.622352000	0.996385000	0.840339000
H	-2.825899000	1.537504000	1.341465000
C	-4.347904000	-0.557318000	-0.846978000
H	-4.117916000	-1.233303000	-1.664676000
C	-4.946445000	1.183572000	1.239886000
H	-5.172992000	1.866191000	2.051454000
C	-5.670104000	-0.372269000	-0.452255000
H	-6.465047000	-0.903837000	-0.963614000
C	-5.973830000	0.498515000	0.595506000
H	-7.003403000	0.644077000	0.902195000
N	1.104025000	-1.402025000	0.139381000
H	0.884522000	-1.094293000	1.080854000
C	2.483097000	-1.475396000	-0.288147000
H	2.651499000	-2.434220000	-0.790434000
C	3.366557000	-1.452048000	0.947003000
O	2.987482000	-1.291768000	2.079080000
C	2.873381000	-0.361915000	-1.309059000
H	3.937062000	-0.468805000	-1.531551000
H	2.315053000	-0.580527000	-2.219783000
C	2.556343000	1.029941000	-0.821720000
C	1.351146000	1.643064000	-1.178818000
H	0.671428000	1.123578000	-1.845177000
C	3.430915000	1.718718000	0.026028000
H	4.376170000	1.262897000	0.302884000
C	1.021282000	2.907670000	-0.695294000
H	0.083127000	3.368160000	-0.985540000
C	3.105464000	2.983282000	0.512417000
H	3.795620000	3.503259000	1.167488000
C	1.897143000	3.580663000	0.155310000
H	1.643770000	4.565248000	0.531905000
O	4.667646000	-1.633344000	0.623350000
H	5.177479000	-1.609599000	1.446963000

### 13. References

1. Abo-Riziq, A.G.; Bushnell, J.E.; Crews, B.; Callahan, M.P.; Grace, L.; De Vries, M.S. Discrimination between diastereoisomeric dipeptides by IR-UV double resonance spectroscopy and ab initio calculations. *Int. J. Quantum Chem.* **2005**, *105*, 437–445, doi:10.1002/qua.20719.
2. Pérez-Mellor, A.; Alata, I.; Lepere, V.; Zehnacker, A. Chirality effects in the structures of jet-cooled bichromophoric dipeptides. *J. Mol. Spectrosc.* **2018**, *349*, 71–84, doi:10.1016/j.jms.2018.02.005.