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

Supplementary Information

Structural Characteristics of Oligomers formed by Pyroglutamate-Modified Amyloid β Peptides Studied by Solid-State NMR

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Scheme S1: Overview of the $^{13}C/^{15}N$-labeled amino acids in the different peptides used in this study. The labeled amino acids are shown in red:

pE3-Aβ(3-40):

1) pEFRHD**S**GY E**V**HHQKLV**F**F AEDVGSNKGA IIG**L**MVGGVV
2) pEFRH**D**S**G**Y EVHHQKLVFF A**E**DVGSNKGA **I**IGLMVGGVV
3) pE**F**RHDSGY **E**VHHQKLVFF AEDVGSNK**G**A IIGLM**V**GGVV

pE11-Aβ(11-40):

1) pE**V**HHQKLV**F**F **A**EDVGSNKGA IIG**L**MV**G**GVV
2) pEVHHQK**L**VFF A**E**DV**G**SNKGA **I**IGLMVGGVV
3) pEVHHQKLVFF AE**D**VGSN**K**GA II**G**LMVGG**V**V
4) **pE**VHHQKLVFF AEDVGSNK**G**A IIGLMVGGVV

Table S1 Isotropic chemical shifts (relative to TMS) for pE_3-Aβ(3-40) Oligomers

Amino Acid	Cα/ ppm	Cβ/ ppm	C=O/ ppm	Cγ/ ppm	Cδ/ ppm	Cε/ ppm	N/ ppm
Phe 4	54.1	36.1/39.7	173.1				n.d.
Asp 7	50.5	38.8	172.0				n.d.
Ser 8	55.5/56.3	62.4/61.9	171.3				120.1
Gly 9	42.4		170.0				n.d.
Glu 11	53.3	31.7	172.4	33.6	180.6		n.d.
Val 12	58.8	31.3/29.9	173.0	19.4			n.d.
Phe 19	54.3	40.2	172.7				118.7
Glu 22	51.7	29.9	171.8	31.2	n.d.		124.2
Gly 29	44.1/42.9[1]		169.1				n.d.
Ile 31	57.7/57.1[1]	39.4	172.0	25.2	15.0	10.8	n.d.
Leu 34	51.6	44.4	172.0	24.2	22.1		120.0.
Val 36	57.7	33.2	172.2	19.0			n.d

[1] two signals observed, strongest signal listed first, n.d.-not detected due to insufficient signal to noise

Table S2 Isotropic chemical shifts (relative to TMS) for pE_{11}-Aβ(11-40) Oligomers

Amino Acid	Cα/ ppm	Cβ/ ppm	C=O/ ppm	Cγ/ ppm	Cδ/ ppm	Cε/ ppm	N/ ppm
pGlu 11	57.1	26.0	174.4	30.2	182.0		125.3
Val 12	58.6/60.3	30.3/31.4	172.7	19.2			n.d.
Leu 17	52.2	44.1	172.8	24.0	24.0		114.1
Phe 19	53.6	44.0	n.r.				124.2
Ala 21	48.4	20.7	n.r.				n.d.
Glu 22	52.7	31.8	173.6	33.1	181.6		117.7
Asp 23	51.8	40.0	173.3	179.2/177.7			124.1
Gly 25	42.8		170.4				110.3
Lys 28	54.0	34.3	174.4	23.0	28.4	39.2	119.7
Gly 29	43.0		169.9				109.0/106.7[1]
Ile 31	58.1	40.2	172.3	26.1	15.4	12.1	114.3
Gly 33	43.2		168.6				111.9
Leu 34	51.4	44.0	n.r.	24.5	25.0		117.2
Gly 37	42.9		170.0				n.d.
Val 39	59.1	28.7	172.3/173.7	19.2			112.5

[1] two signals observed, strongest signal listed first, n.d.-not detected due to insufficient signal to noise, n.r. –not resolved in 2D spectrum

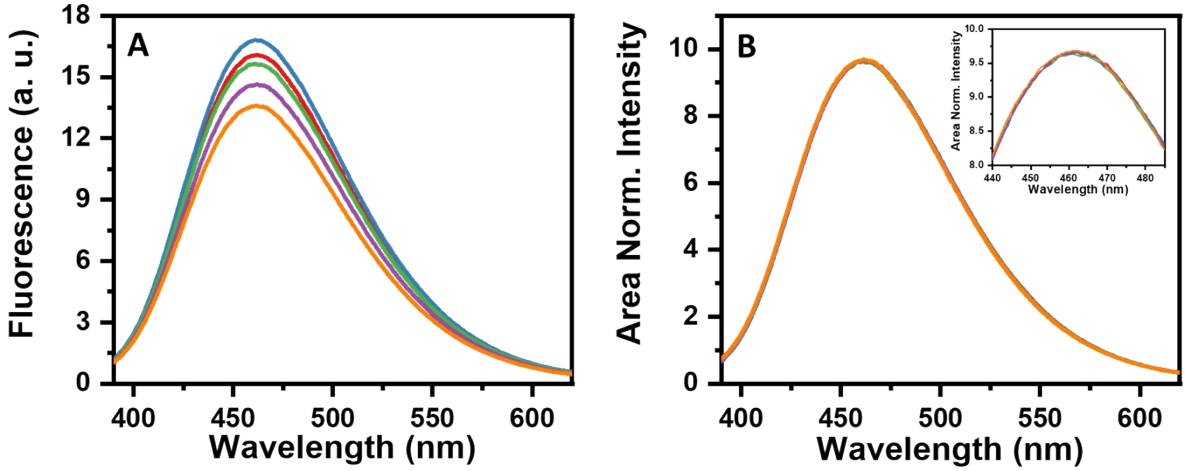

Figure S1: Fluorescence emission of TPE-TPP as a function of time, when incubated with WT-Aβ(1-40). (A) shows the emission spectra at 5 different time points, at an interval of 30 mins, t = 0 (red), 30 mins (blue), 1 hr (green), 1.5 hrs (purple) and 2 hours (orange). (B) Same data as in panel A, area normalized, inset shows the zoomed in version of (B).

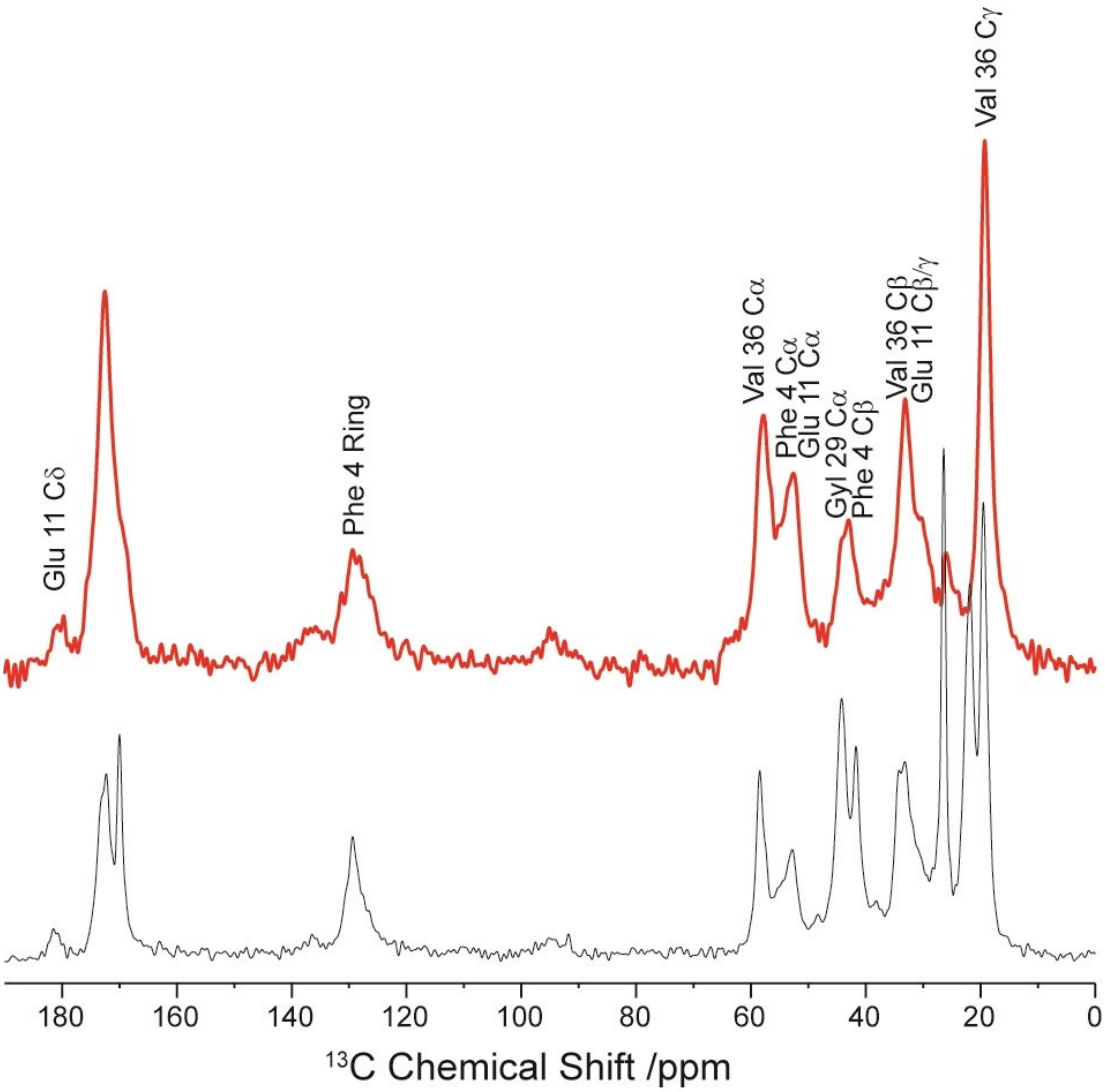

Figure S2: Example of the ^{13}C CP MAS NMR spectra of oligomers (above) and mature fibrils (below) of pE_3-Aβ(3-40) peptide II at a MAS frequency of 11777 Hz and a temperature of 30°C. The spectrum of the mature fibrils was taken from [1].

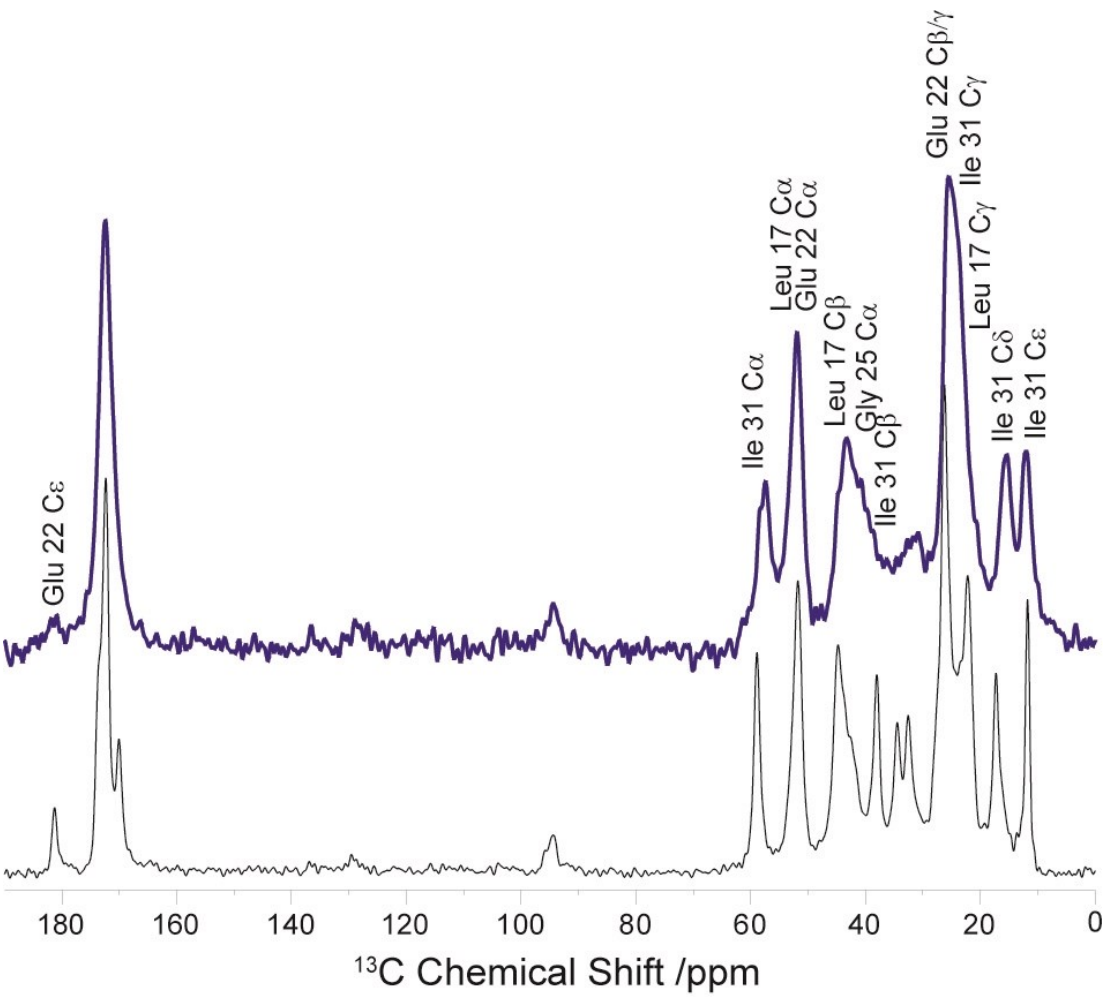

Figure S3: Example of the ^{13}C CP MAS NMR spectra of oligomers (above) and mature fibrils (below) of pE_{11}-Aβ(11-40) peptide V at a MAS frequency of 11777 Hz and a temperature of 30°C. The spectrum of the mature fibrils was taken from [2].

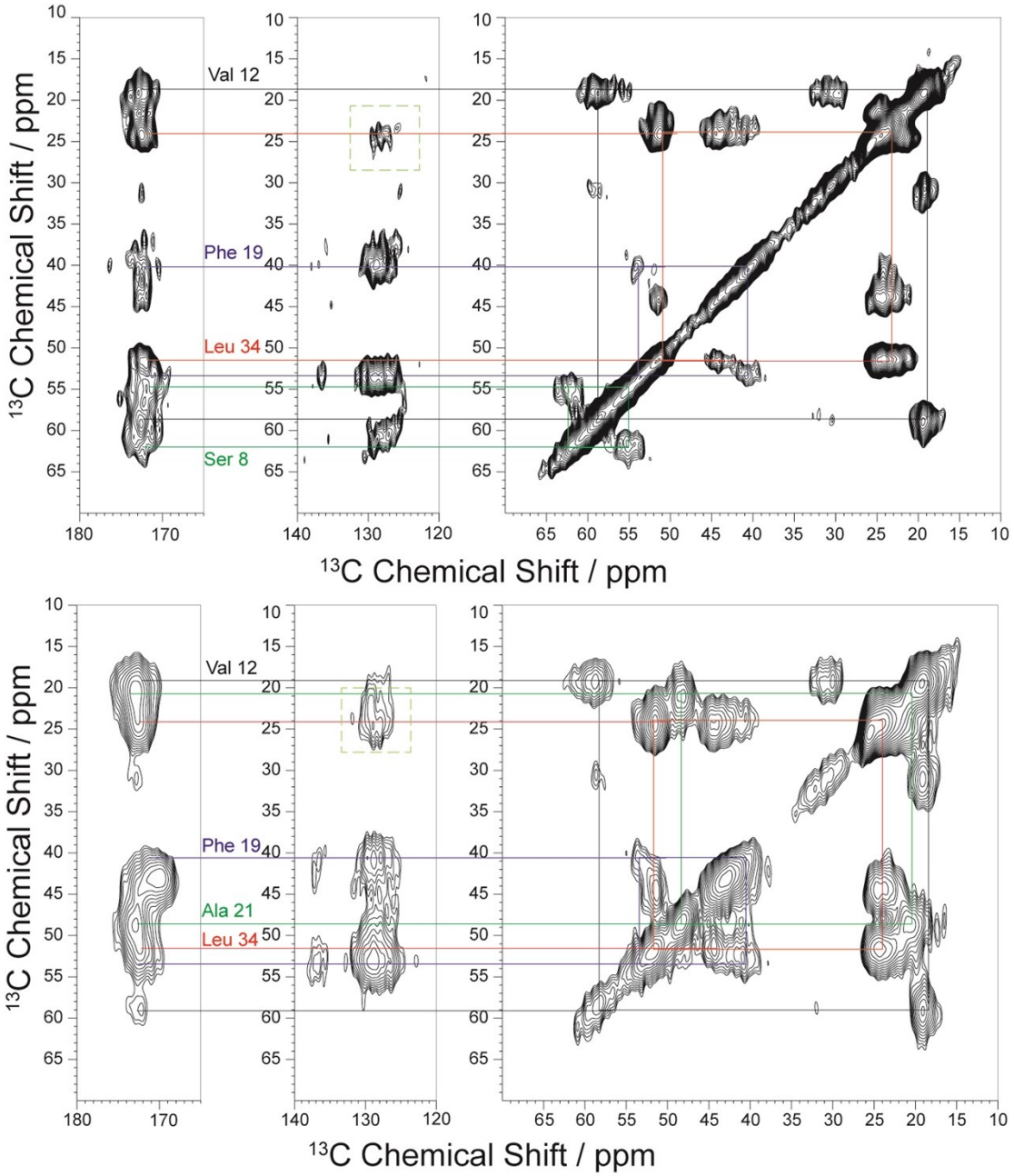

Figure S4: ^{13}C-^{13}C DARR MAS NMR spectra of oligomers of $pGlu_3$-Aβ(3-40) peptide I (above) and $pGlu_{11}$-Aβ(11-40) peptide IV (below) with a DARR mixing time of 500 ms at a MAS frequency of 11,777 Hz and a temperature of 30°C with the respective assignment. The green boxes indicate interresidual crosspeaks between Phe_{19} and Leu_{34}.

References:

[1] H. A. Scheidt, J. Adler, M. Krueger and D. Huster, *Sci. Rep.*, 2016, **6**, 33531.

[2] H. A. Scheidt, J. Adler, U. Zeitschel, C. Hofling, A. Korn, M. Krueger, S. Rossner and D. Huster, *Chemistry.*, 2017, **23**, 15834-15838.