Electronic Supplementary Information

Hierarchical approach for the rational construction of helix-containing nanofibrils using α,β-peptides

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Table S1. Peptides analytical data.

Name	Formula	$M_{cal.}$[a]	M_{MS}[b]	M_{TFA}[c]	HPLC $t_{ret.}$ [min][d]
1	$C_{125}H_{202}N_{32}O_{35}$	2713.13 [1/2M+1] 1357.26 [1/3M+1] 905.18	 [1/2M+1] 1357.26 [1/3M+1] 905.18	3055.22	17.053
1_a	$C_{125}H_{196}N_{32}O_{35}$	2707.08 [1/2M+1] 1354.24 [1/3M+1] 903.16 [1/4M+1] 677.62	 [1/2M+1] 1354.30 [1/3M+1] 903.50 [1/4M+1] 677.65	3049.17	16.260
1_b	$C_{134}H_{214}N_{32}O_{35}$	2833.32 [1/2M+1] 1417.31 [1/3M+1] 945.21 [1/4M+1] 709.16	 [1/2M+1] 1417.31 [1/3M+1] 945.21 [1/4M+1] 709.18	3175.41	17.660
1_c	$C_{134}H_{214}N_{32}O_{35}$	2833.32 [1/2M+1] 1417.31 [1/3M+1] 945.21	 [1/2M+1] 1417.33 [1/3M+1] 945.21	3175.41	17.440
1_d	$C_{125}H_{196}N_{32}O_{35}$	2707.08 [1/2M+1] 1354.24 [1/3M+1] 903.16 [1/4M+1] 677.62	 [1/2M+1] 1354.26 [1/3M+1] 903.16 [1/4M+1] 677.64	3049.17	16.200
1_e	$C_{125}H_{193}N_{29}O_{35}$	2662.04 [1/2M+1] 1331.72 [1/3M+1] 888.15 [1/4M+1] 666.36	 [1/2M+1] 1331.76 [1/3M+1] 887.83	2662.04	16.733
1_f	$C_{130}H_{208}N_{30}O_{33}$	2719.22 [1/2M+1] 1360.29 [1/3M+1] 907.19	 [1/2M+1] 1360.28 [1/3M+1] 907.19	3061.31	17.173
1_g	$C_{128}H_{208}N_{32}O_{29}$	2659.21 [1/2M+1] 1330.30 [1/3M+1] 887.20 [1/4M+1] 665.65	 [1/2M+1] 1330.33 [1/3M+1] 887.20 [1/4M+1] 665.66	3001.30	16.467

[a] $M_{cal.}$ – calculated mass of the peptide

[b] M_{MS} – found mass of the peptide using HRMS

[c] M_{TFA} –actual mass of the peptide taking under account presence of TFA counterion

[d] HPLC $t_{ret.}$ – retention time in analytical HPLC spectra

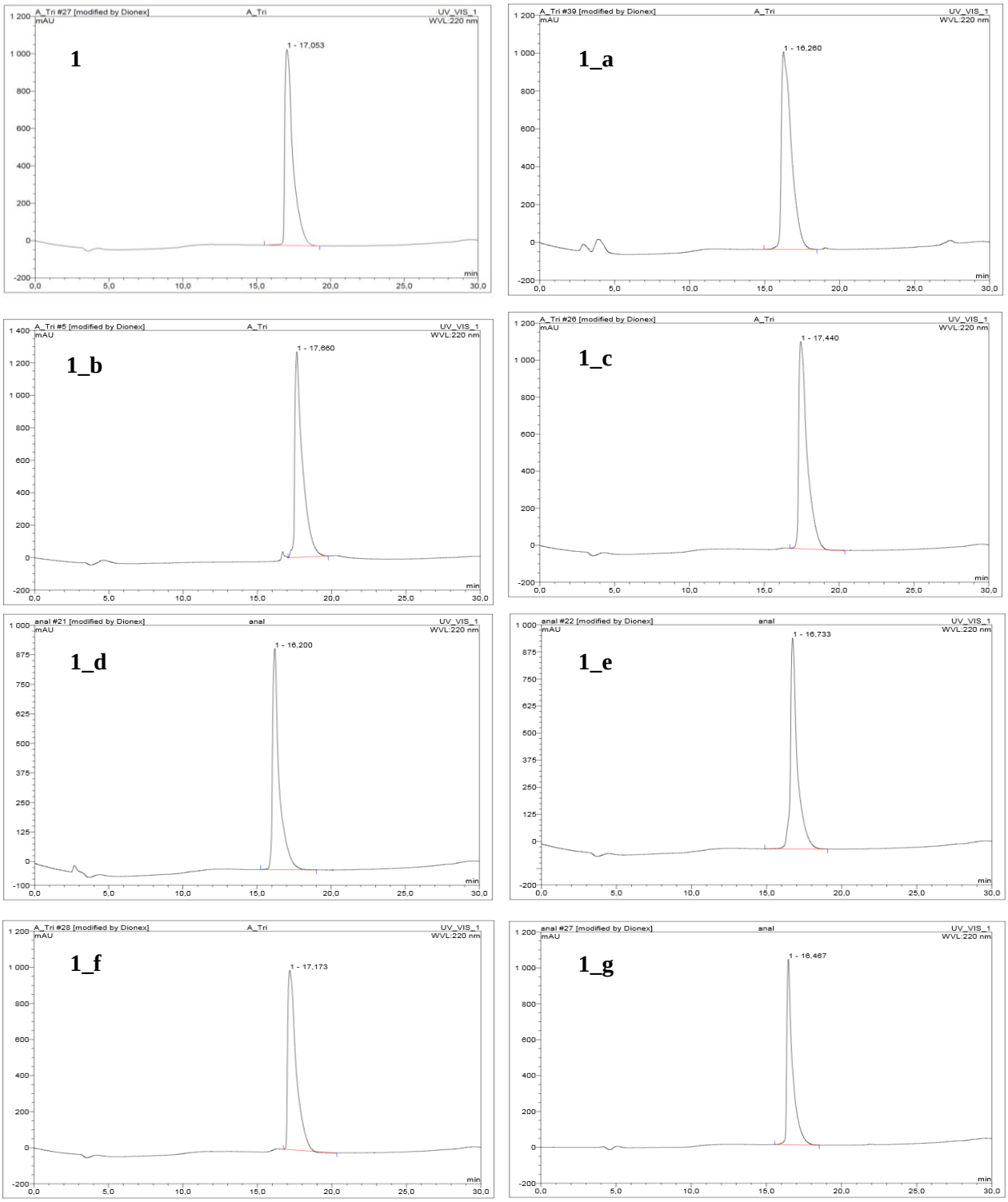

Figure S2. Analytical HPLC chromatograms of studied peptides.

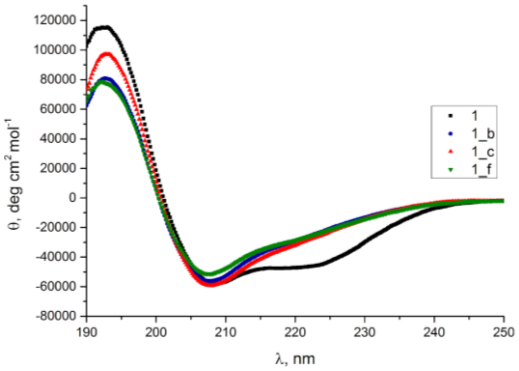

Figure S3_1. CD spectra of studied peptides dissolved in MeOH ($c_{peptide}$ = 80 μM).

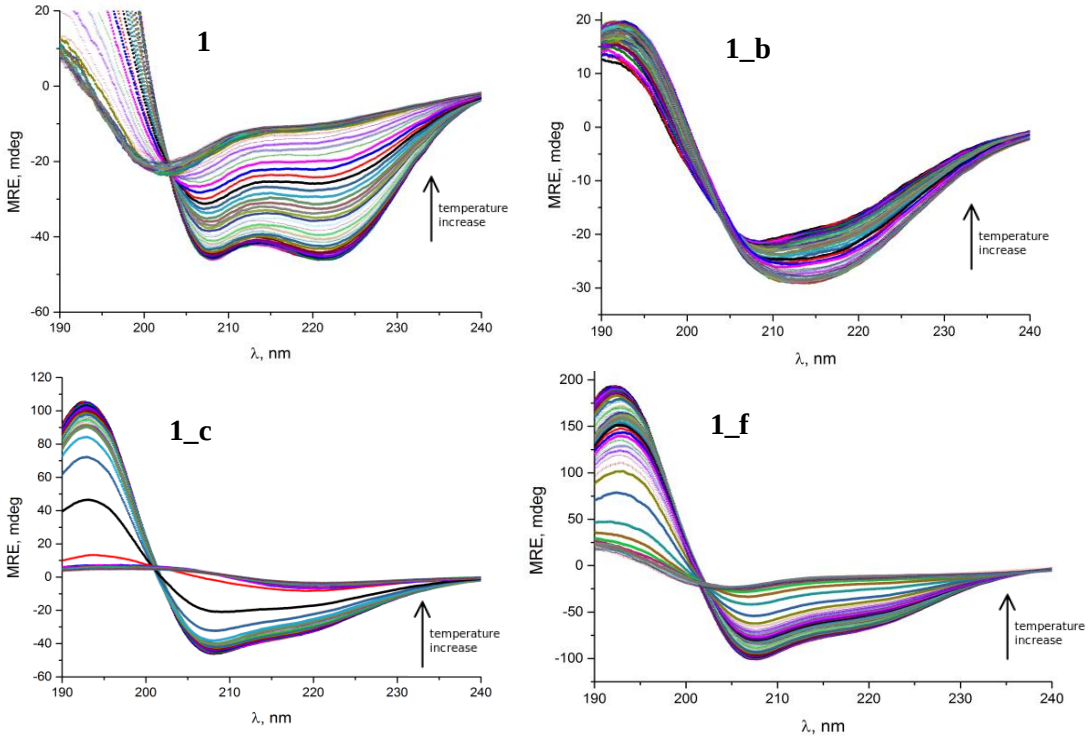

Figure S3_2. CD spectra recorded in temperature range 4 – 98 ºC ($c_{peptide}$ = 80 μM in water, pH 7).

Table S3_3. The melting temperatures of studied peptides measured at 222 nm.

Name	T, ºC
1	56.4 ± 0.3
1_c	76.4 ± 0.4
1_f	70.5 ± 0.5

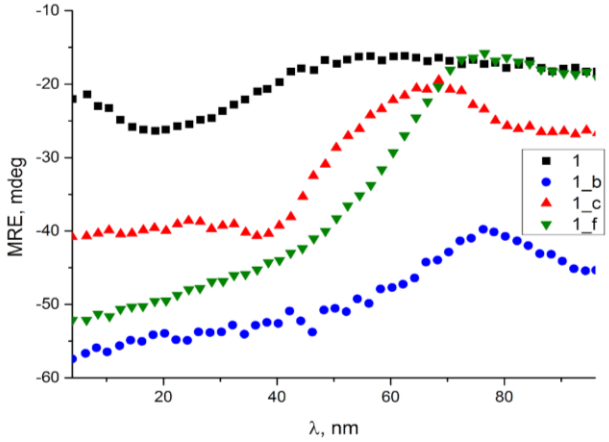

Figure S3_4. Thermal denaturation curves of studied peptide in the presence of 3 M guanidine hydrochloride measured at 222 nm ($c_{peptide}$ = 80 μM in water, pH 7).

Table S4. NMR chemical shifts and interproton contacts obtained from spectra of studied peptides.

1_b

Residue	Proton	Chemical shift [ppm]
Ac1	HA	2.09
Gly2	HN	8.68
	HA	3.79; 4.00
Glu3	HN	8.72
	HA	4.31
	HB	2.10
	HG	2.50
Ile4	HN	7.75
	HA	3.93
	HB	1.98
	HG1	1.31; 1.65
	HG2	0.99
	HD	0.96
Cp5	HN	7.47
	HA	2.60
	HB	4.37
	HG,D,E	1.77; 1.87; 1.97; 2.02
Ala6	HN	8.06
	HA	4.05
	HB	1.53
Ile7	HN	8.08
	HA	3.80
	HB	2.35
	HG1	1.23; 1.93
	HG2	0.97
	HD	0.93
Lys8	HN	8.22
	HA	3.96
	HB	1.99; 2.02
	HG	1.49
	HD	1.69; 1.76
	HE	2.93
	NH_3Z	7.89
Gln9	HN	8.53
	HA	4.05
	HB	2.09; 2.35
	HG	2.56
	GNH_2	7.40; 6.76
Glu10	HN	8.30
	HA	4.20
	HB	2.21; 2.41
	HG	2.46; 2.66
Ile11	HN	8.32
	HA	3.81
	HB	1.91
	HG1	1.28; 1.87
	HG2	0.96
	HD	0.88
Cp12	HN	7.97
	HA	2.83
	HB	4.37
	HG,D,E	1.77; 1.82; 1.92
Ala13	HN	8.21
	HA	4.08
	HB	1.66
Ile14	HN	8.53
	HA	3.81
	HB	2.39
	HG1	1.18
	HG2	0.98
	HD	0.93
Lys15	HN	8.26
	HA	3.93
	HB	1.94
	HG	1.35; 2.02
	HD	1.60; 1.72
	HE	2.81
	NH_3Z	7.84
Trp16	HN	8.57
	HA	4.42
	HB	3.34; 3.41
	HD1	7.17
	HE	7.58
	HZ1	7.02
	HZ2	7.34
	HH	7.10
	NH	10.24
Glu17	HN	8.52
	HA	4.20
	HB	2.27; 2.49
	HG	2.73
Ile18	HN	8.39
	HA	3.81
	HB	1.93
	HG1	1.27; 1.87
	HG2	0.94
	HD	0.88
Cp19	HN	7.96
	HA	2.89
	HB	4.36
	HG,D,E	1.69; 1.82; 1.92
Ala20	HN	8.31
	HA	3.98
	HB	1.53
Ile21	HN	8.50
	HA	3.84
	HB	2.41
	HG1	1.84
	HG2	0.98
	HD	0.94
Lys22	HN	8.40
	HA	4.09

	HB	2.01
	HG	1.56
	HD	1.68
	HE	2.93
	NH_3Z	7.81
Gln23	HN	8.49
	HA	4.20
	HB	2.18; 2.53
	HG	2.35;2.53
	GNH_2	7.39; 6.76
Gly24	HN	8.20
	HA	3.89
Tyr25	HN	8.08
	HA	4.51
	HB	2.94; 3.16
	HD	7.17
	HE	6.71
Gly26	HN	8.16
	HA	3.84; 3.88
NH_2	HN1	7.17
	HN2	7.40

Sequential (*i*, *i*-1)	**Intensity**
HN2 – HA1	s
HN3 – HA2	m
HN4 – HA3	w
HN5 – HA4	w
HN6 – HA5	s
HN7 – HA6	w
HN8 – HA7	w
HN9 – HA8	w
HN10 – HA9	w
HN11 – HA10	w
HN12 – HA11	w
HN13 – HA12	s
HN14 – HA13	w
HN15 – HA14	w
HN16 – HA15	w
HN17 – HA16	w
HN18 – HA17	w
HN19 – HA18	w
HN20 – HA19	s
HN21 – HA20	w
HN22 – HA21	w
HN23 – HA22	m
HN24 – HA23	w
HN25– HA24	w
HN26 – HA25	0

HN-HN	**Intensity**
HN3 – HN4	m
HN4 – HN5	m
HN5 – HN6	w
HN8 – HN9	m
HN9 – HN10	m
HN11 – HN12	m
HN14 – HN15	w
HN15 – HN16	m
HN16 – HN17	m
HN18 – HN19	m
HN19 – HN20	w
HN20 – HN21	w
HN21 – HN22	m
HN23 – HN24	m
HN24 – HN25	w

Medium range (*i*, *i*+2)	**Intensity**
HB12 – HN14	w
HA14 – HN16	w

Medium range (*i*, *i*+3)	**Intensity**
HA3 – HN6	w
HA3 – HB6	w
HA4 – HB7	w
HB5 – HN8	m
HA7 – HB10	w
HA7 – HG10	w
HA7 – HN10	w
HA8 – HN11	w
HA9 – HA12	w
HA9 – HN12	w
HA10 – HB13	w

HB12 – HN15	m
HA13 – HB16	w
HA13 – HN16	w
HA14 – HN17	w
HA15 – HN18	w
HA17 – HB20	w
HB19 – HN22	m
HA20 – HB23	w

Medium range (*i*, *i*+4)	**Intensity**
HA8 – HN12	w
HA15 – HN19	w
HB19 – HN23	w
HN20 – HA16	w

NH	**^{3}J [Hz]**
HN1	0
HN2	5.31
HN3	5.42
HN4	6.84
HN5	8.90
HN6	7.79*
HN7	8.39*
HN8	*
HN9	*
HN10	*
HN11	5.27
HN12	8.48
HN13	*
HN14	*
HN15	1.81
HN16	4.41
HN17	*
HN18	6.22*
HN19	8.06
HN20	*
HN21	*
HN22	*
HN23	6.35
HN24	*
HN25	6.40*
HN26	5.98

(*) overlapping signals were observed, hence the determined coupling constants may be affected by an error or it was impossible to determine them

1_c

Residue	**Proton**	**Chemical shift [ppm]**
Ac1	HA	2.08
Gly2	HN	8.79
	HA	3.79; 3.99
Glu3	HN	8.91
	HA	4.22
	HB	2.12
	HG	2.53; 2.58
Ile4	HN	7.87
	HA	3.93
	HB	2.14
	HG1	1.32
	HG2	1.00
	HD	0.95
Ala5	HN	7.36
	HA	4.03
	HB	1.44
Cp6	HN	7.75
	HA	2.72
	HB	4.40
	HG,D,E	1.70; 1.78; 1.99
Ile7	HN	8.23
	HA	3.72
	HB	2.14
	HG1	1.40
	HG2	0.99
	HD	0.99
Lys8	HN	8.39
	HA	3.96
	HB	2.00; 2.07
	HG	1.46
	HD	1.69; 1.83
	HE	2.92
	NH_3Z	7.87
Gln9	HN	8.00
	HA	4.09
	HB	2.26; 2.32
	HG	2.37; 2.56
	GNH_2	6.77; 7.39
Glu10	HN	8.62
	HA	4.08
	HB	2.14; 2.44
	HG	2.44; 2.71
Ile11	HN	8.38
	HA	3.85
	HB	2.78
	HG1	1.23
	HG2	0.98
	HD	0.90
Ala12	HN	8.33

	HA	4.03
	HB	1.54
Cp13	HN	8.22
	HA	3.01
	HB	4.66
	HG,D,E	1.74; 1.83; 1.93; 2.05
Ile14	HN	8.45
	HA	3.75
	HB	2.23
	HG1	1.31
	HG2	1.00
	HD	1.00
Lys15	HN	8.83
	HA	3.97
	HB	2.32
	HG	1.48; 1.72
	HD	2.85; 2.02
	HE	2.93
	NH_3Z	7.87
Trp16	HN	8.03
	HA	4.29
	HB	3.45; 3.61
	HD1	2.86
	HE	2.79
	HZ1	2.84
	HZ2	2.85
	HH	2.89
	NH	10.34
Glu17	HN	8.88
	HA	3.74
	HB	2.13; 2.43
	HG	2.43; 2.70
Ile18	HN	8.24
	HA	3.76
	HB	2.01
	HG1	1.19
	HG2	0.92
	HD	0.89
Ala19	HN	8.21
	HA	3.87
	HB	1.39
Cp20	HN	8.21
	HA	2.58
	HB	4.08
	HG,D,E	1.25; 1.39; 1.45; 1.57
Ile21	HN	8.44
	HA	3.69
	HB	2.17
	HG1	1.25
	HG2	0.96
	HD	0.96
Lys22	HN	8.38
	HA	4.09
	HB	2.06; 2.13
	HG	1.49
	HD	1.68
	HE	2.91
	NH_3Z	7.89
Gln23	HN	7.98
	HA	4.13
	HB	2.17; 2.26
	HG	2.36; 2.50
	GNH_2	6.72; 7.46
Gly24	HN	8.32
	HA	3.83
Tyr25	HN	7.92
	HA	4.47
	HB	2.93; 3.13
	HD	7.14
	HE	6.70
Gly26	HN	8.15
	HA	3.79; 3.90
NH_2	HN1	7.15
	HN2	7.33

Sequential (*i*, *i*-1)	**Intensity**
HN2 – HA1	s
HN3 – HA2	m
HN4 – HA3	w
HN5 – HA4	w
HN6 – HA5	w
HN7 – HA6	s
HN8 – HA7	w
HN9 – HA8	w
HN10 – HA9	*
HN11 – HA10	w
HN12 – HA11	w
HN13 – HA12	w
HN14 – HA13	s
HN15 – HA14	w
HN16 – HA15	w
HN17 – HA16	m
HN18 – HA17	*
HN19 – HA18	m
HN20 – HA19	*
HN21 – HA20	s
HN22 – HA21	w
HN23 – HA22	m
HN24 – HA23	w
HN25– HA24	m

HN26 – HA25	w

HN-HN	Intensity
HN3 – HN4	m
HN4 – HN5	m
HN5 – HN6	m
HN6 – HN7	w
HN7 – HN8	m
HN8 – HN9	m
HN9 – HN10	m
HN10 – HN11	m
HN11 – HN12	m
HN12 – HN13	m
HN13 – HN14	w
HN14 – HN15	m
HN15 – HN16	m
HN16 – HN17	m
HN17 – HN18	m
HN20 – HN21	w
HN22 – HN23	m
HN23 – HN24	m
HN24 – HN25	m
HN25 – HN26	m
HN26 – $(NH_2)1$	w
HN26 – $(NH_2)2$	w

Medium range (*i*, *i*+2)	Intensity
HB6 – HN8	w
HA8 – HN10	w
HB13 – HN15	w
HA14 – HN16	w
HA15 – HN17	w

Medium range (*i*, *i*+3)	Intensity
HA3 – HA6	w
HA3 – HN6	w
HA4 – HN7	w
HA5 – HN8	m
HB6 – HB9	w
HA6 – HN9	m
HA7 – HB10	w
HA7 – HN10	m
HA8 – HA11	w
HA9 – HN12	w
HA10 – HA13	w
HA11 – HB14	w
HA12 – HB15	w
HA12 – HD15	w
HA11 – HN14	m
HA12 – HN15	m
HA13 – HN16	m
HA15 – HN18	m
HA16 – HB19	w
HA16 – HN19	m
HA19 – HB22	w

Medium range (*i*, *i*+4)	Intensity
HA3 – HN7	w
HB6 – HN10	w
HA8 – HN12	w
HA10 – HN14	w
HA11 – HN15	w
HA13 – HN17	w
HA15 – HN19	w
HA18 – HN22	w
HA21 – HN25	w

NH	^3J [Hz]
HN1	0
HN2	5.07
HN3	4.69
HN4	~7.43*
HN5	5.32
HN6	9.43
HN7	*
HN8	*
HN9	4.41
HN10	4.31
HN11	*
HN12	~4*

HN13	~9.17*
HN14	*
HN15	3.04
HN16	3.79
HN17	3.17

HN18	~5.1*
HN19	*
HN20	~9.54*
HN21	*
HN22	*

HN23	5.93
HN24	~6.40*
HN25	7.46
HN26	5.93

1_f

Residue	Proton	Chemical shift [ppm]
Ac1	HA	2.07
Gly2	HN	8.71
	HA	3.78; 4.00
Glu3	HN	8.85
	HA	4.20
	HB	2.08; 2.13
	HG	2.52
Ile4	HN	7.96
	HA	3.83
	HB	2.10
	HG1	1.36
	HG2	1.00
	HD	1.00
Ala5	HN	7.50
	HA	4.06
	HB	1.50
Ala6	HN	7.86
	HA	4.07
	HB	1.55
Ile7	HN	7.92
	HA	3.90
	HB	2.01
	HG1	1.23
	HG2	0.99
	HD	0.91
Lys8	HN	8.12
	HA	3.93
	HB	1.83; 1.91
	HG	1.42
	HD	1.67
	HE	2.91
	NH_3Z	7.85
Cp9	HN	8.04
	HA	2.81
	HB	4.43
	HG,D,E	1.75; 1.78; 1.86, 1.90
Glu10	HN	8.20
	HA	4.03
	HB	2,37; 2.45
	HG	2.62
Ile11	HN	8.81
	HA	3.74
	HB	2.36
	HG1	1.20
	HG2	0.98
	HD	0.90
Ala12	HN	7.93
	HA	4.04
	HB	1.58
Trp13	HN	8.62
	HA	4.43
	HB	3.40
	HD1	7.13
	HE	7.59
	HZ1	7.02
	HZ2	7.34
	HH	7.10
	NH	10.20
Ile14	HN	8.50
	HA	3.86
	HB	2.13
	HG1	1.24
	HG2	1.00
	HD	0.97
Lys15	HN	8.46
	HA	3.93
	HB	1.83; 1.87
	HG	1.44
	HD	1.66
	HE	2.91
	NH_3Z	7.85
Cp16	HN	8.09
	HA	2.93
	HB	4.39
	HG,D,E	1.70; 1.87; 2.00
Glu17	HN	8.40
	HA	3.88
	HB	2.24; 2.30
	HG	2.38; 2.42
Ile18	HN	8.78
	HA	3.68
	HB	2.32
	HG1	1.16
	HG2	0.94
	HD	0.90

Ala19	HN	7.99
	HA	3.99
	HB	1.56
Ala20	HN	8.60
	HA	4.05
	HB	1.53
Ile21	HN	8.22
	HA	3.85
	HB	2.04
	HG1	1.22
	HG2	1.01
	HD	0.93
Lys22	HN	8.29
	HA	4.09
	HB	1.90
	HG	1.50
	HD	1.65
	HE	2.89
	NH_3Z	7.78
Cp23	HN	7.95
	HA	2.85
	HB	4.31
	HG,D,E	1.74; 1.85; 1.94; 2.01
Gly24	HN	8.31
	HA	3.76; 3.85
Tyr25	HN	8.06
	HA	4.60
	HB	3.06; 3.31
	HD	7.19
	HE	6.69
Gly26	HN	8,27
	HA	3.78; 3.99
NH_2	HN1	7.35
	HN2	7.56

Sequential (*i*, *i*-1)	**Intensity**
HN2 – HA1	m
HN3 – HA2	s
HN4 – HA3	w
HN5 – HA4	w
HN6 – HA5	w
HN7 – HA6	w
HN8 – HA7	w
HN9 – HA8	w
HN10 – HA9	s
HN11 – HA10	w
HN12 – HA11	w
HN13 – HA12	m
HN14 – HA13	w
HN15 – HA14	w
HN16 – HA15	w
HN17 – HA16	s
HN18 – HA17	w
HN19 – HA18	w
HN20 – HA19	w
HN21 – HA20	w
HN22 – HA21	w
HN23 – HA22	w
HN24 – HA23	s
HN25 – HA24	w
HN26 – HA25	w

HN-HN	**Intensity**
HN3 – HN4	m
HN4 – HN5	m
HN5 – HN6	m
HN7 – HN8	m
HN8 – HN9	m
HN9 – HN10	w
HN10 – HN11	m
HN11 – HN12	m
HN12 – HN13	m
HN13 – HN14	m
HN14 – HN15	m
HN15 – HN16	m
HN16 – HN17	w
HN17 – HN18	m
HN18 – HN19	m
HN19 – HN20	m
HN20 – HN21	m
HN22 – HN23	m
HN23 – HN24	w
HN24 – HN25	w
HN25 – HN26	m

Medium range (*i*, *i*+2)	**Intensity**
HA3 – HN5	w

HA11 – HN13	w
HA12 – HN14	w
HA13 – HN15	w
HA18 – HN20	w

Medium range (*i*, *i*+3)	**Intensity**
HA3 – HB6	w
HA3 – HN6	m
HA4 – HB7	w
HA4 – HD7	w
HA4 – HN7	m
HA5 – HN8	m
HA6 – HA9	w
HA6 – $CH_2$9	w
HA6 – HN9	m
HA8 – HB11	w
HA8 – HN11	m
HB9 – HB12	w
HB9 – HN12	s
HA10 – HB13	w
HA10 – H(D1)13	w
HA11 – HB14	w
HA11 – HN14	m
HA12 – HB15	w
HA12 – HN15	m
HA14 – HG17	w
HA15 – HB18	w
HA15 – HD18	w
HA15 – HN18	m
HB16 – HB19	w
HB16 – HN19	s
HA17 – HB20	w
HA17 – HN20	m
HA18 – HB21	w
HA18 – HN21	m
HA19 – HB22	w
HA20 – $CH_2$23	w
HA20 – HA23	w
HA22 – HN25	w
HA22 – HD25	w
HA22 – HB25	w
HB23 – HN26	w

Medium range (*i*, *i*+4)	**Intensity**
HA2 – HN6	w
HA3 – HN7	w
HA4 – HN8	w
HA11 – HN15	w
HA12 – HN16	w
HA13 – HN17	w
HA15 – HN19	w
HA18 – HN22	w
NH_2(2) – HN23	m
NH_2(1) – HN23	w

NH	**^{3}J [Hz]**
HN1	0
HN2	5.16
HN3	4.26
HN4	4.74
HN5	4.91
HN6	4.36
HN7	5.63*
HN8	4.25
HN9	10.03
HN10	1.93*
HN11	3.71
HN12	~3*
HN13	4.67
HN14	5.21
HN15	4.20
HN16	9.82
HN17	2.03*
HN18	3.71
HN19	3.11
HN20	4.05
HN21	5.87*
HN22	4.17*
HN23	8.40
HN24	5.31
HN25	8.16
HN26	6.25*

A

B

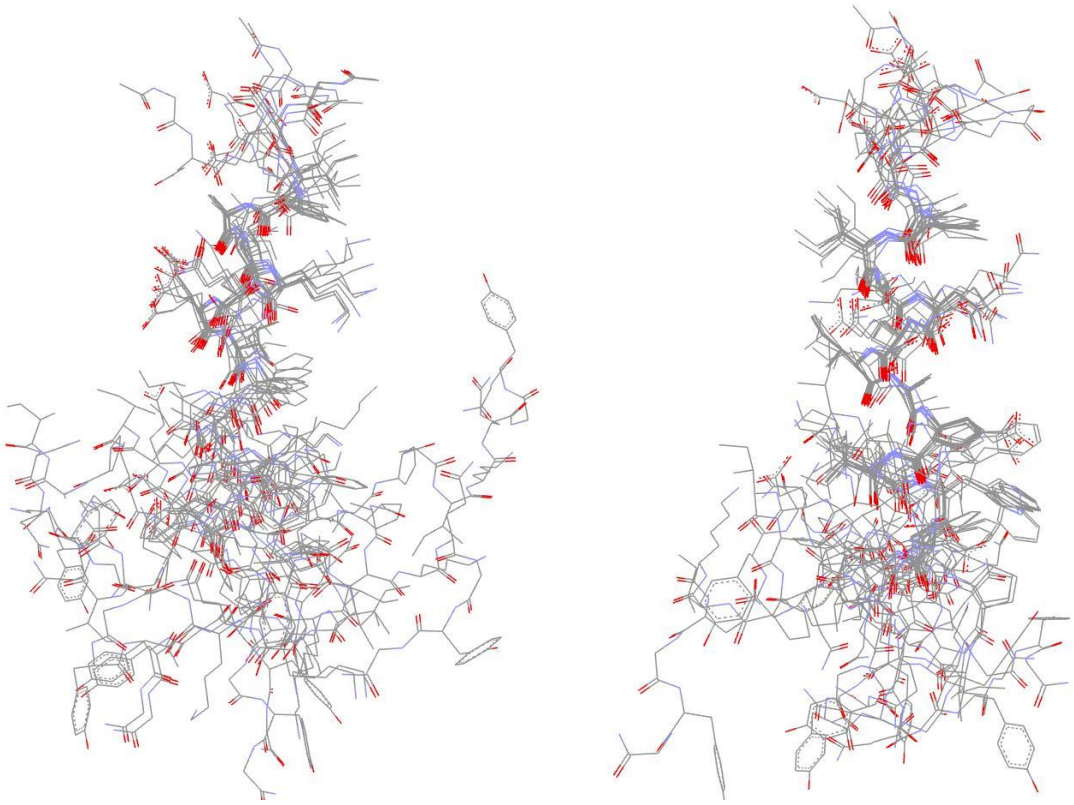

Figure S4_1. Superimposition of 10 lowest energy structures of obtained for peptides **1_b** (A) and **1_c** (B) using molecular dynamics with NMR restrains.

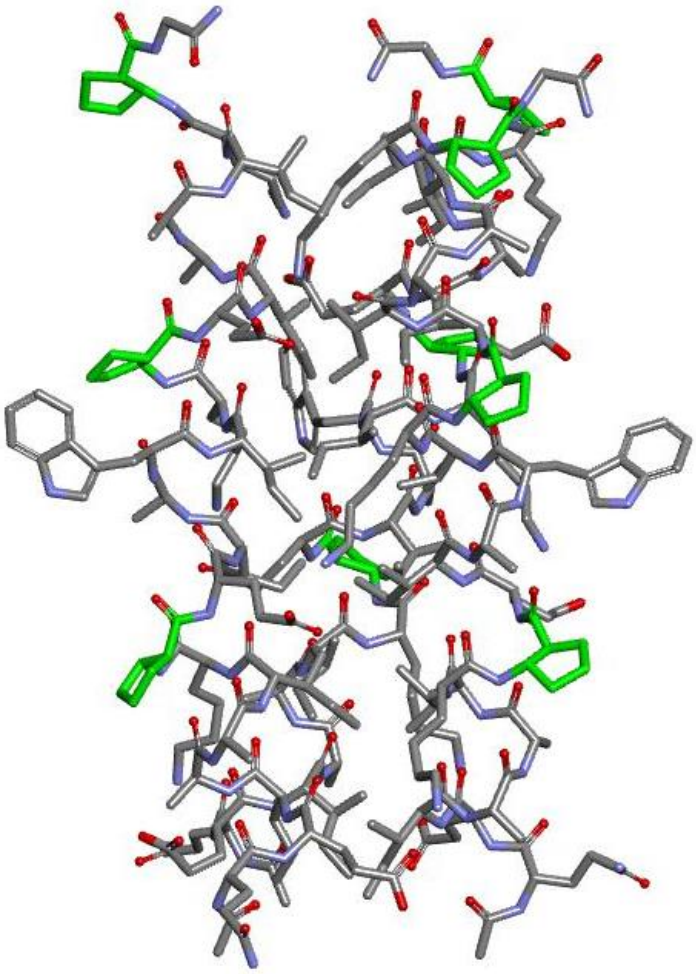

Figure S4_2. Modelled structure of trimeric coiled coil formed by peptide **1_f**. β-Amino acid residues are shown as stick with carbon atoms colored in green.

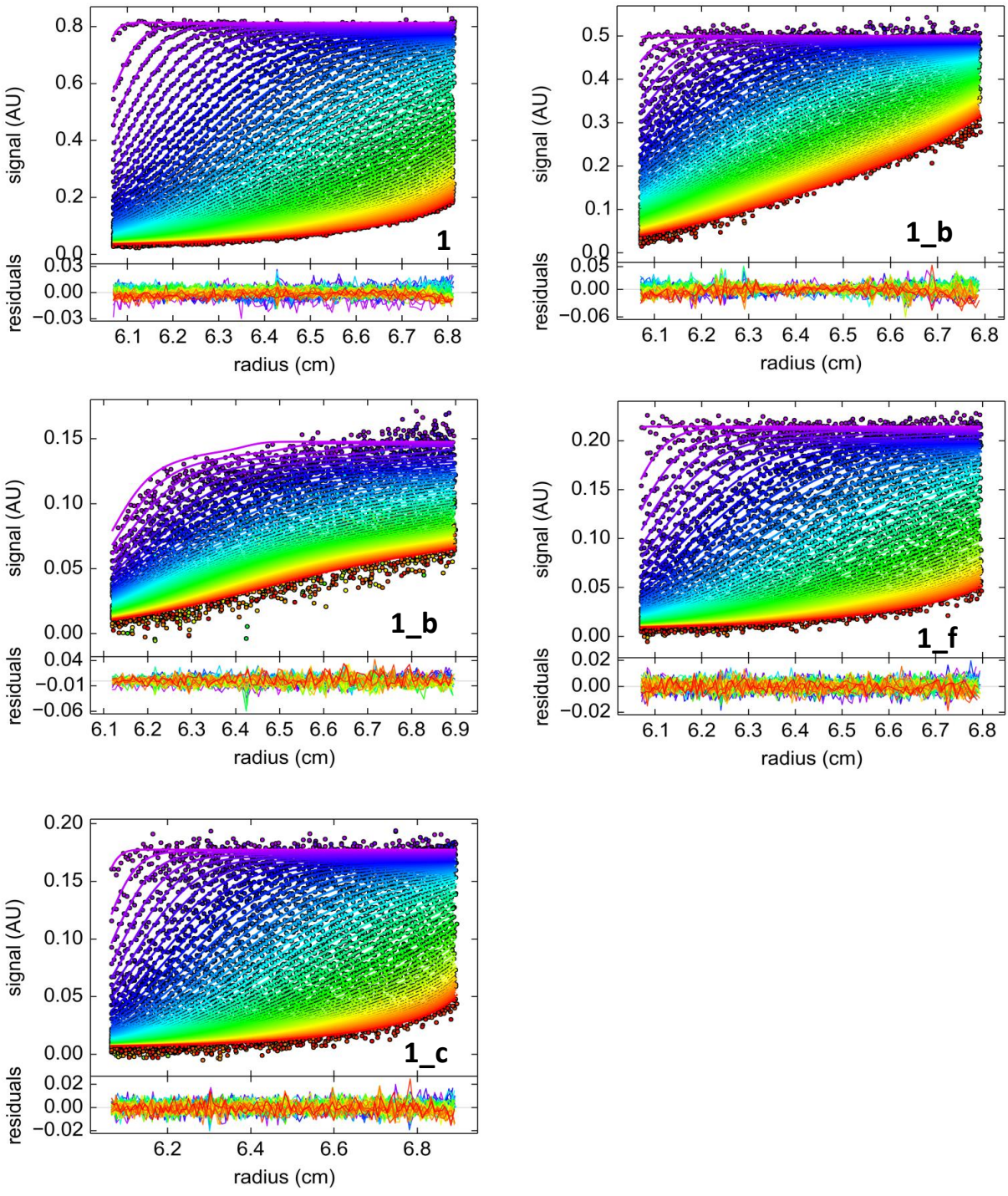

Figure S5_1. Radial absorption profiles at 280 nm (•) registered every 5 or 10 min, with the best fits of SEDFIT *c*(*s*) model (—) for peptide **1** (100 μM), **1_b** (80 μM) and **1_c** (40 μM) in AUC buffer (left panels), and for peptide **1_b** (80 μM) and **1_f** (30 μM) in H_2O (right panels). Every second or fourth profile is shown for clarity.

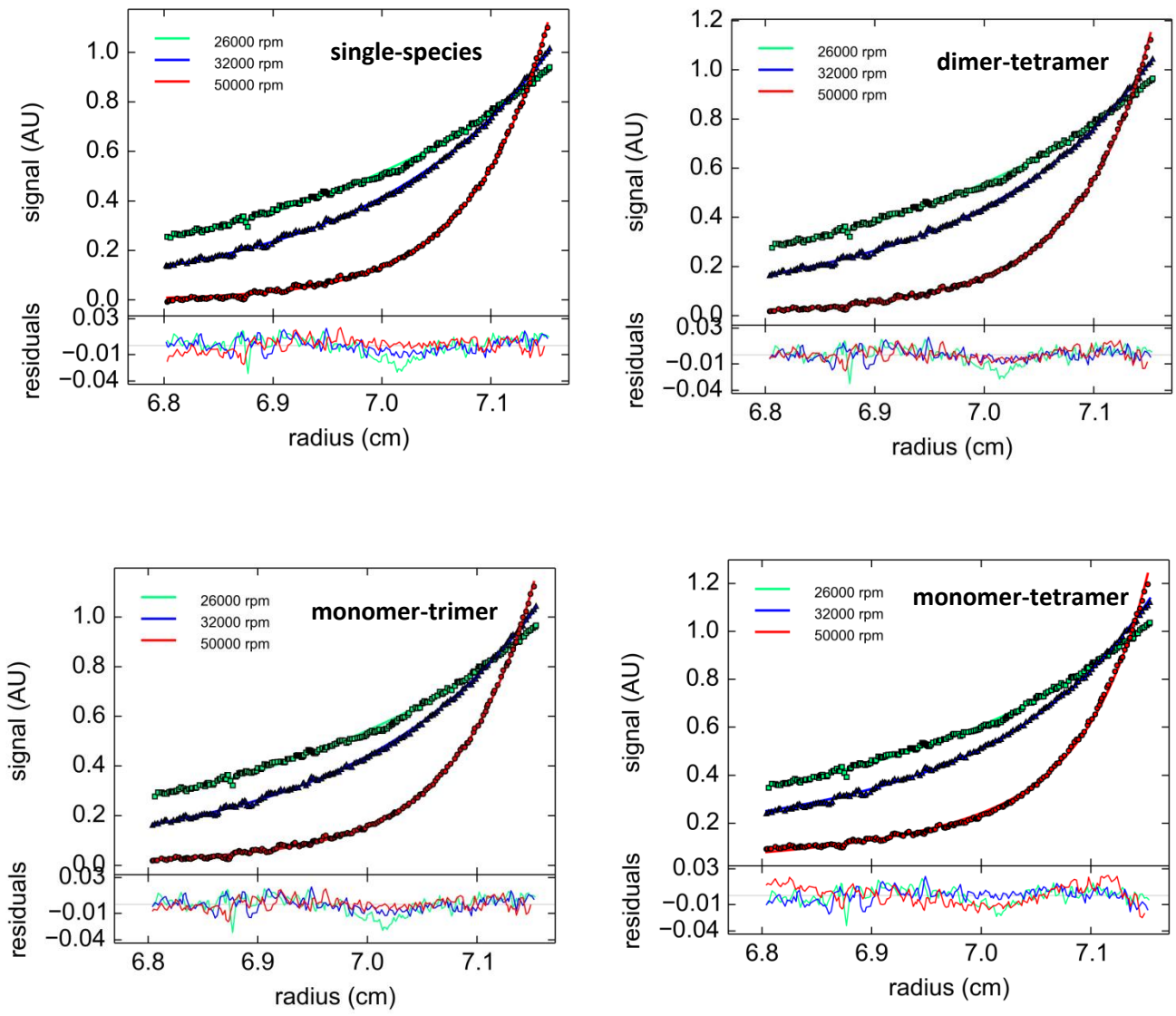

Figure S5_2. Sedimentation equilibrium gradients for peptide **1** (75 μM) in AUC buffer for the rotor speeds of 26000 (■), 32000 (▲), and 50000 rpm (•). The best global fits (—) of a single species model as well as several monomer-*n*-mer self-association models in SEDPHAT are shown with the fitting residuals (bottom panel).

Table S5_3. Parameters resulting from the analysis of sedimentation equilibrium data[a], obtained for the peptide **1** (75 μM) in AUC buffer, according to the single species and various self-association models (monomer-*n*-mer or monomer-*n*-mer-*m*-mer).

model	M [b] [Da]	n/m	K_{d12} [μM]	K_{d23}/ K_{d24} [μM]	K_d* [μM] [c]	χ^2
single species	7 717 ± 22					2.904396
monomer-dimer	2713	2	$(3.2 \pm 2.2)\cdot 10^{-5}$			24.182180
monomer-trimer	2713	3			6.8 ± 0.5	2.582851
monomer-tetramer	2713	4			65 ± 1	3.364030
dimer-tetramer	5426	2	77 ± 2			2.380125
monomer-dimer-trimer	2713	2/3	$\sim 10^{22}$	$\sim 10^{-21}$		2.582852
monomer-dimer-tetramer	2713	2/4	0.10 ± 0.14	71 ± 219		2.380522

[a] equilibrium constants for monomer-*n*-mer or monomer-*n*-mer-*m*-mer association (K_{a1n}, or K_{a1n} and K_{a1m}) were fitted parameters; dissociation constants K_{d12}, K_{d23} and K_{d24} were obtained from the relationships $K_{dnm} = 1/K_{anm}$ and from $K_{a23} = K_{a13}/K_{a12}$ and $K_{a24} = K_{a14}/(K_{a12})^2$

[b] molecular mass was a fitted parameter in the single species model, and was fixed in self-association models

[c] effective dissociation constant $K_d^* = K_{a1n}^{(-1/n-1)}$ for monomer-*n*-mer association (equals the free monomer concentration where $c_1 = c_n$, where c_1 is monomer concentration and c_n is *n*-mer concentration)

Table S5_4. Partial specific volumes $\bar{v}$ of peptides calculated from the partial specific volumes obtained in Sednterp, $\bar{v}_{ST}$, and partial specific volumes of the *trans*-ACPC residues and the end groups (Ac and NH_2) obtained according to the method of Durchschlag and Zipper.

peptide	$\bar{v}_{ST}$ (cm^3/g)[a]	$\bar{v}$ (cm^3/g)
1	0.76367	0.76617
1_b	0.76592	0.77389
1_c	0.76592	0.77389
1_f	0.77501	0.78206

[a] the partial specific volumes obtained in Sednterp from amino acid composition of peptide, excluding *trans*-ACPC residues, acetyl group at the N-terminus and NH_2 group at the C-terminus

Table S5_5. Theoretical values of sedimentation coefficients in the standard conditions ($s_{20,w}$) for various oligomeric forms of peptides **1**, **1_b**, **1_c** and **1_f** calculated as described in Experimental Section.

n-mer	$s_{20,w}$ (S)			
	1	1_b	1_c	1_f
1	0.484	0.354	0.467	0.454
2	0.768	0.562	0.742	0.721
3	**1.006**	**0.737**	**0.972**	**0.945**
4	1.219	0.893	1.177	1.145
5	1.414	1.036	1.366	1.328
6	1.597	1.170	1.543	1.500

Table S6. The fluorescence intensity of the studied peptides in relation to fluorescence intensity of ThT alone and kinetic parameters of fibril formation obtained using Tht fluorescence assay.

Sample	**Relative fluorescence [-]**	**t_{lag} [min]**	**$t_{1/2}$ [min]**	**τ [min]**
1	20.5	-	-	-
1_b	5830.6	240	390	75
1_c	268.7	120	300	90
1_f	119.4	-	-	-

Table S7_1. Tentative assignments of main bands presented in vibrational spectra of studied peptides in powder form.

1		**1_b**		**1_c**		**1_f**		**Assignment**	
band position [cm^{-1}]									
Raman	ATR-FTIR	Raman	ATR-FTIR	Raman	ATR-FTIR	Raman	ATR-FTIR		
3296	3290	3308	3294	3295	3287	3293	3289	Amide A	**ν(NH)**
3062	3053	3060	3055	3059	3059	3061	3052	Amide B	**ν(NH)**
	2966		-		2964		2964	aa	ν(CH_2)
2937	2937	2934	2938	2936	2936	2936	2935	aa	ν(CH_3,CH_2)
2880	2877	2880	2875	2878	2877	2879	2876	aa	ν(CH_2)
2855	-	2855	-	2855	-	2855	-	aa	ν(CH_3)
1654	**1651**	**1652**	**1646**	**1651**	**1643**	**1652**	**1648**	**Amide I**	**ν(CO), ν(NH)**
1554	-	1555	-	1555	-	1556	-	W	W3
-	**1542**	**-**	**1539**	**-**	**1534**	**-**	**1538**	**Amide II**	**δ(NH) , ν(CN)**
1456	1456	1451	1454	1449	1453	1458	1458	aa	δ(CH_2)
1360		1358	-	-	-	1360	-	W	Fermi doublet, W7
1340		1338	-	1339	-	1338	-	W	Fermi double, W7
1322	**-**	**1321**	**-**	**1321**	**-**	**1321**	**-**	**Amide III**	**ν(CN) , δ(NH)**
	1201		1200		1200		1201	W,Y	ν(CC)
1176	1179	-	1180	1169	1175	1175	1176	Y	Y9
1130	1136	1129	1134	1129	1134	1129	1136	Y	ν(CC)
1105	-	1105	-		-	1108	-		ν(CC)
1011	-	1010	-	1010	-	1011	-	Y, W	$\Delta(CC)_{ring}$,W16
991	-	987	-	987	-	984	-		ν(CC)
927	-	934	-	927	-	927	-		ν(CC)
886	-	882	-		-	877	-	W	W17
850	-	851	-	851	-	850	-	Y	Fermi doublet, Y1
830	835	834	834		835	830	835	Y	Fermi doublet, Y1
	800		799		799		799		δ(CH_2)
757	-	759	742	759	-	757	742	W	W18
722	**722**	**721**	**721**	**723**	**721**	**722**	**721**	**Amide IV**	**δ(CH_2), δCO**
643	-	642	-	643	-	643	-	Y, W	$\delta(CC)_{ring}$

Abbreviations: ν, stretching; δ, deformation; Δ - benzene ring breathing mode, aa - amino acid side chains, W - tryptophan, Y – tyrosine.

Table S7_2. Amide band positions in vibrational spectra of studied peptides in powder form.

1		**1_b**		**1_c**		**1_f**		**Assignment**	
band position [cm^{-1}]									
Raman	ATR-FTIR	Raman	ATR-FTIR	Raman	ATR-FTIR	Raman	ATR-FTIR		
3296	3290	3308	3294	3295	3287	3293	3289	Amide A	**ν(N-H)**
3062	3053	3060	3055	3059	3059	3061	3052	Amide B	**ν(N-H)**
1654	**1651**	**1652**	**1646**	**1651**	**1643**	**1652**	**1648**	**Amide I**	**ν(C=O) 80%, ν(NH) 20%**
-	1542	-	1539	-	1534	-	1538	Amide II	**δ (N-H) 60%,ν(C-N) 40%**,
1322	-	1321	-	1321	-	1321	-	Amide III	**ν(C-N) 40%, δ(N-H) 30%**

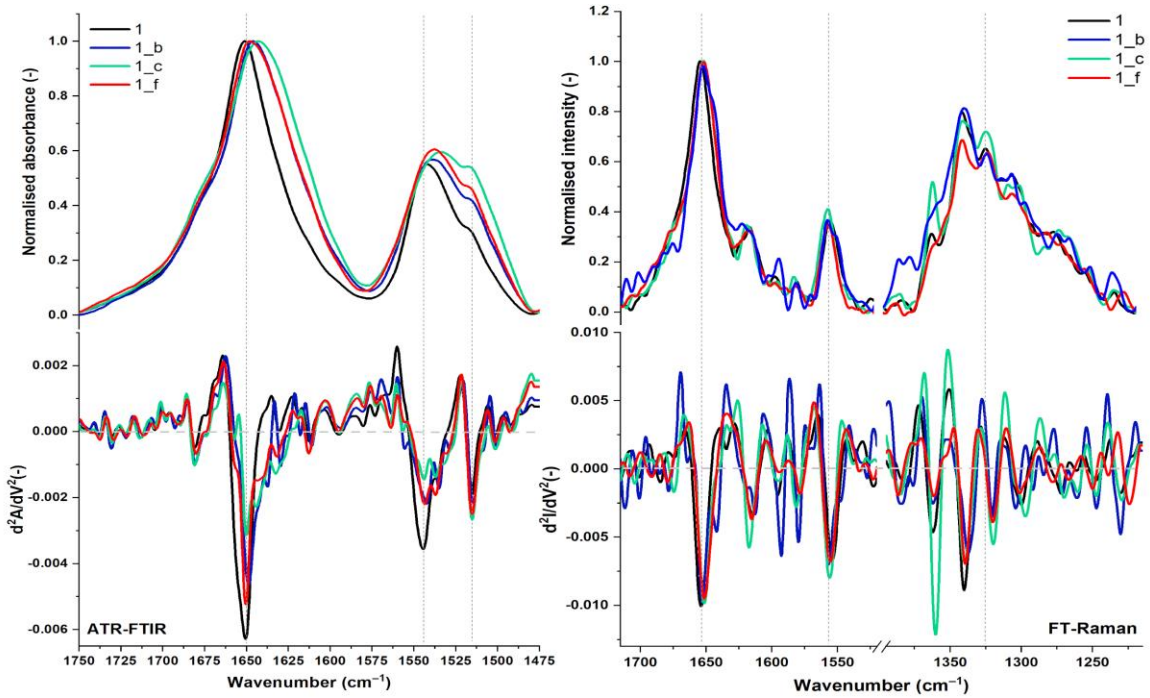

Figure S7_3. (left) Normalized ATR-FTIR spectra of peptides in amide I and II range (1750 – 1475 cm^{-1}) with second derivatives. (right) Normalized FT-Raman spectra of peptides in amide I and III range (1750 – 1210 cm^{-1}) with second derivatives.

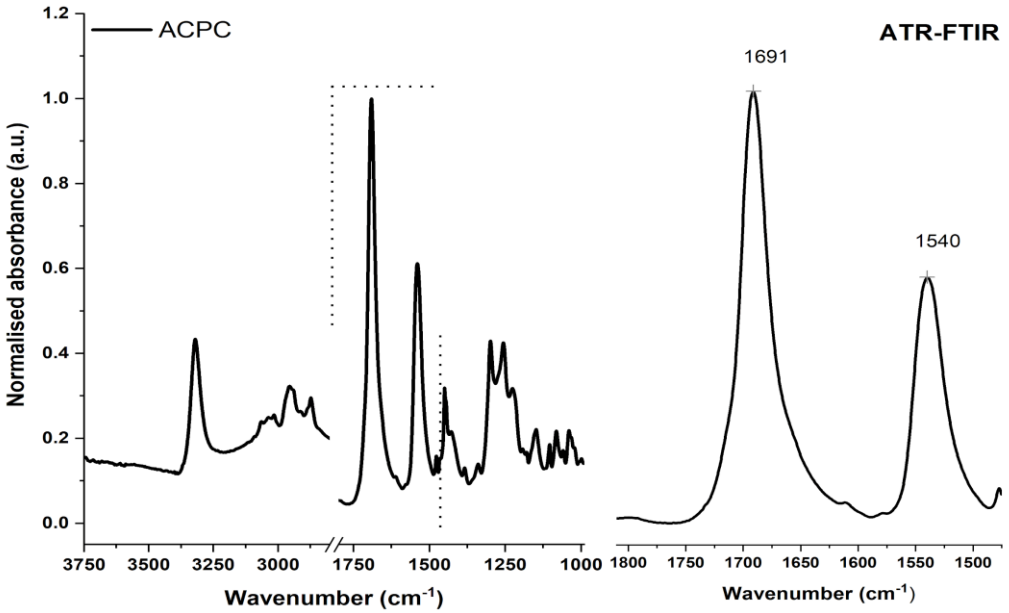

Figure S7_4. Normalized ATR-FTIR spectra of *trans*-2-aminocyclopentanecarboxylic acid (*trans*-ACPC) in powder form.

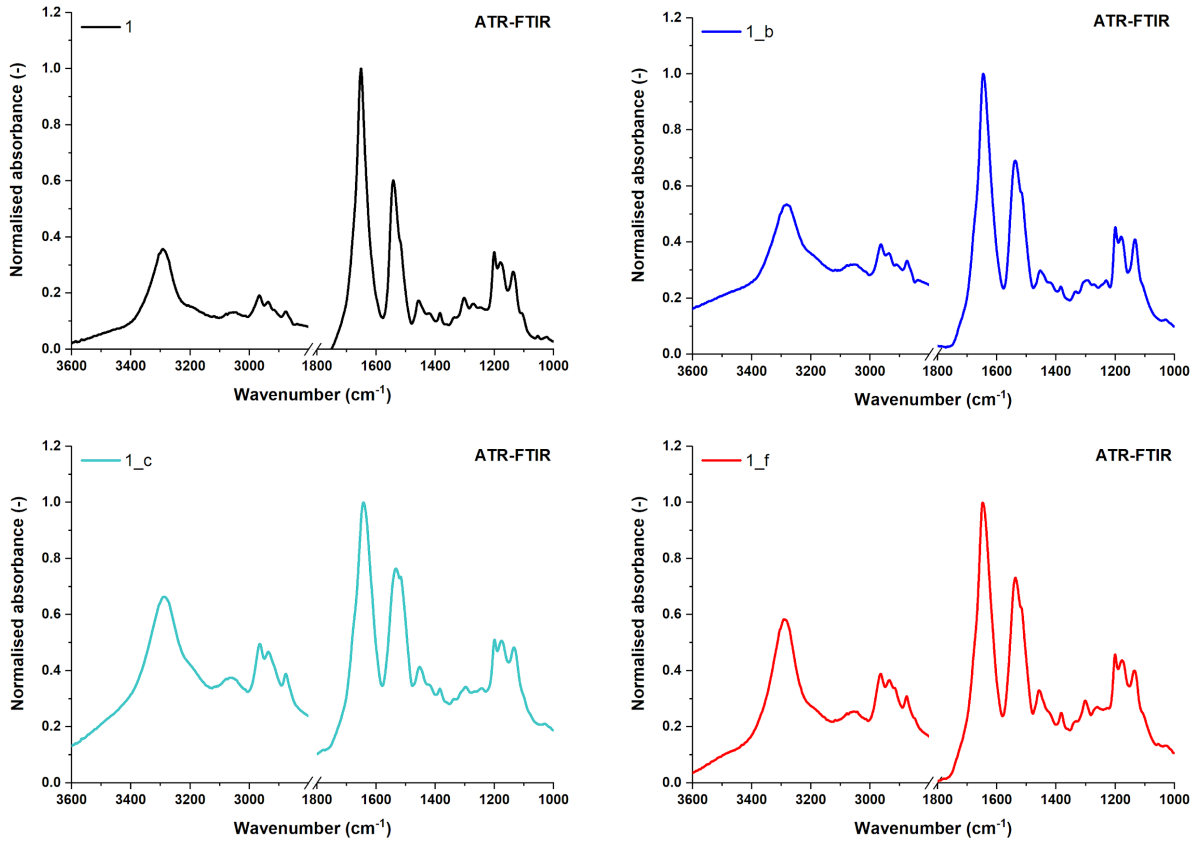

Figure S7_5. Normalized ATR-FTIR spectra of studied peptides in powder form.

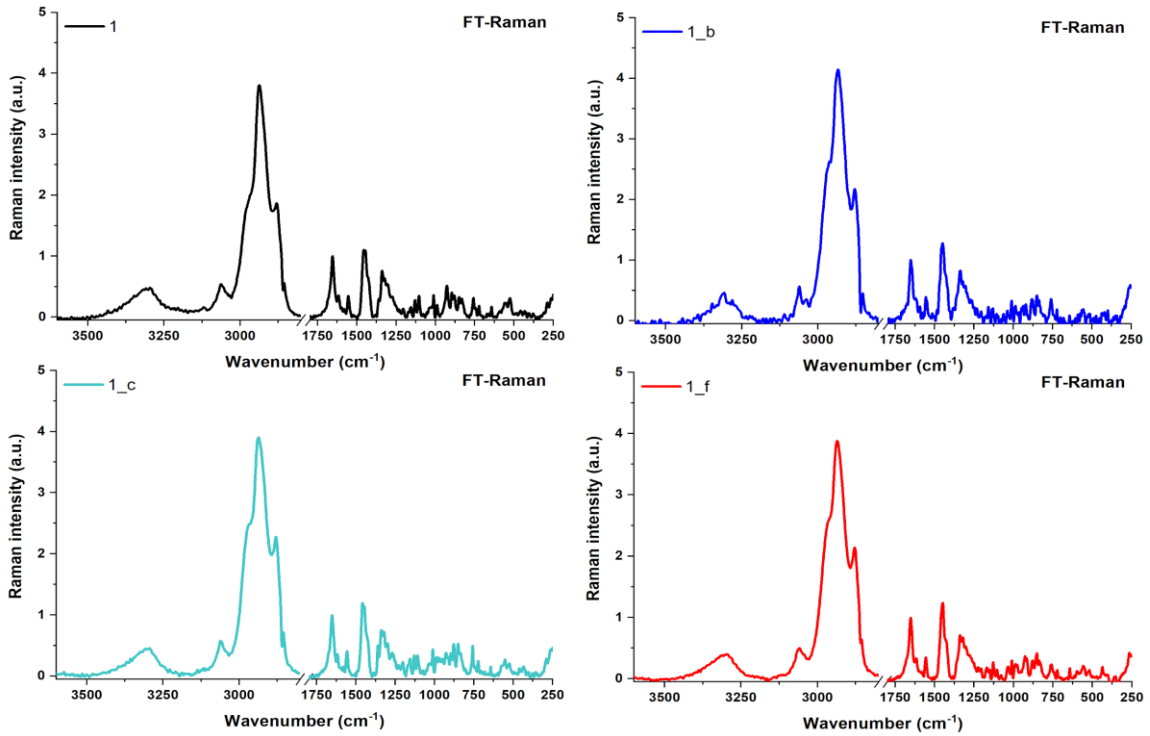

Figure S7_6. Normalized FT-Raman spectra of studied peptides in powder form.

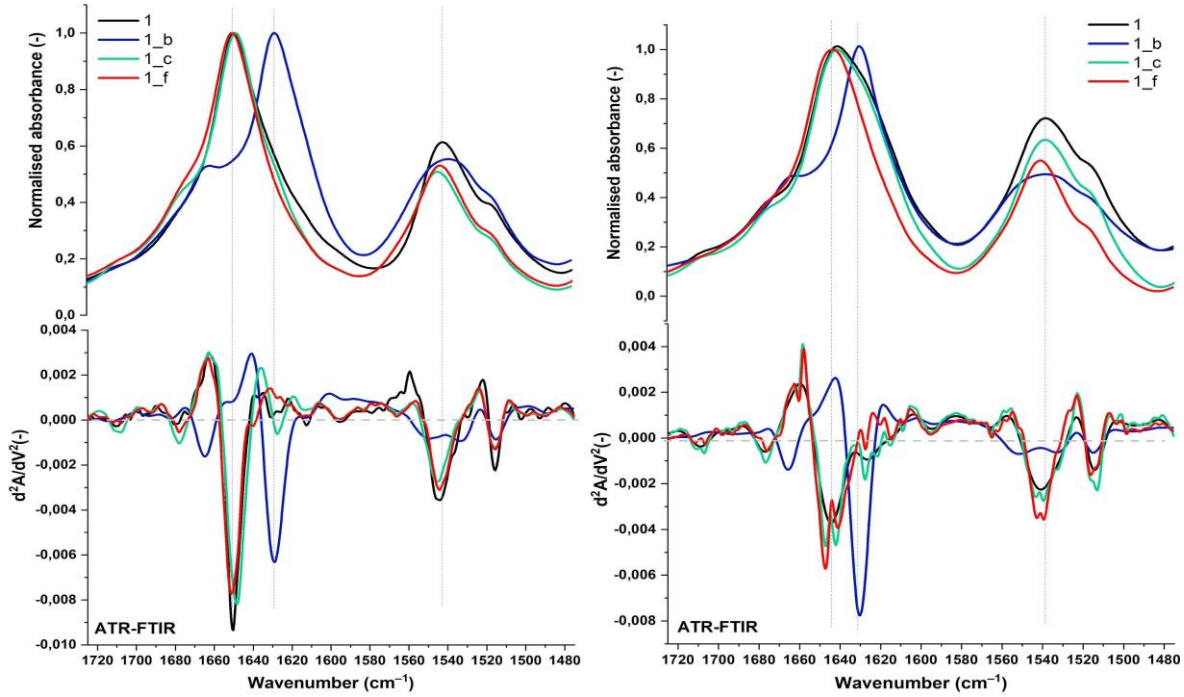

Figure S7_7. (left) Normalized ATR-FTIR spectra of 1.3 mM peptides solutions in water in amide I and II range (1725 – 1475 cm^{-1}) with second derivatives. (right) Normalized ATR-FTIR spectra of 1.3 mM peptides solutions in water in amide I and II range (1750 – 1475 cm^{-1}) with second derivatives after 7 days of incubation.

Table S7_8. Amide band positions in ATR-FTIR spectra of 1.3 mM peptides solutions in water before and after 7 days of incubation.

1		**1_b**		**1_c**		**1_f**		**Assignment**
band position [cm^{-1}]								
0 days	**7 days**	0 days	**7 days**	0 days	**7 days**	0 days	**7 days**	
3294	3278	3300	3297	3298	3298	3296	3278	Amide A
3060	3077	3060	3061	3059	3059	3061	3076	Amide B
1648	-	1646/**1628**	**1653**	**1648**	**1650**	**1649**	**1641**	**Amide I**
1542	1545	1539	1545	1534	1543	1538	1539	Amide II

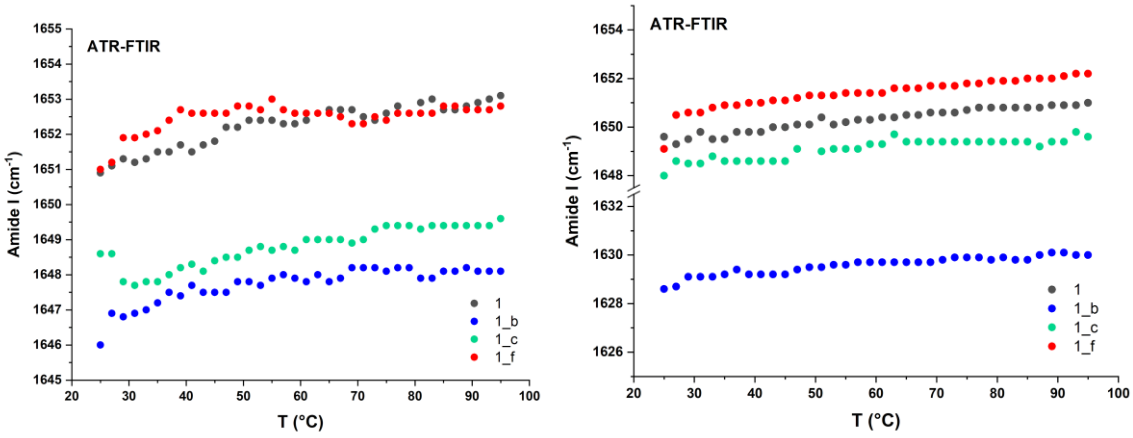

Figure S7_9. Temperature dependence ATR-FTIR spectra of peptides in powder form (left) and in 1.3 mM solutions in water (right) (amide I position as a function of temperature).

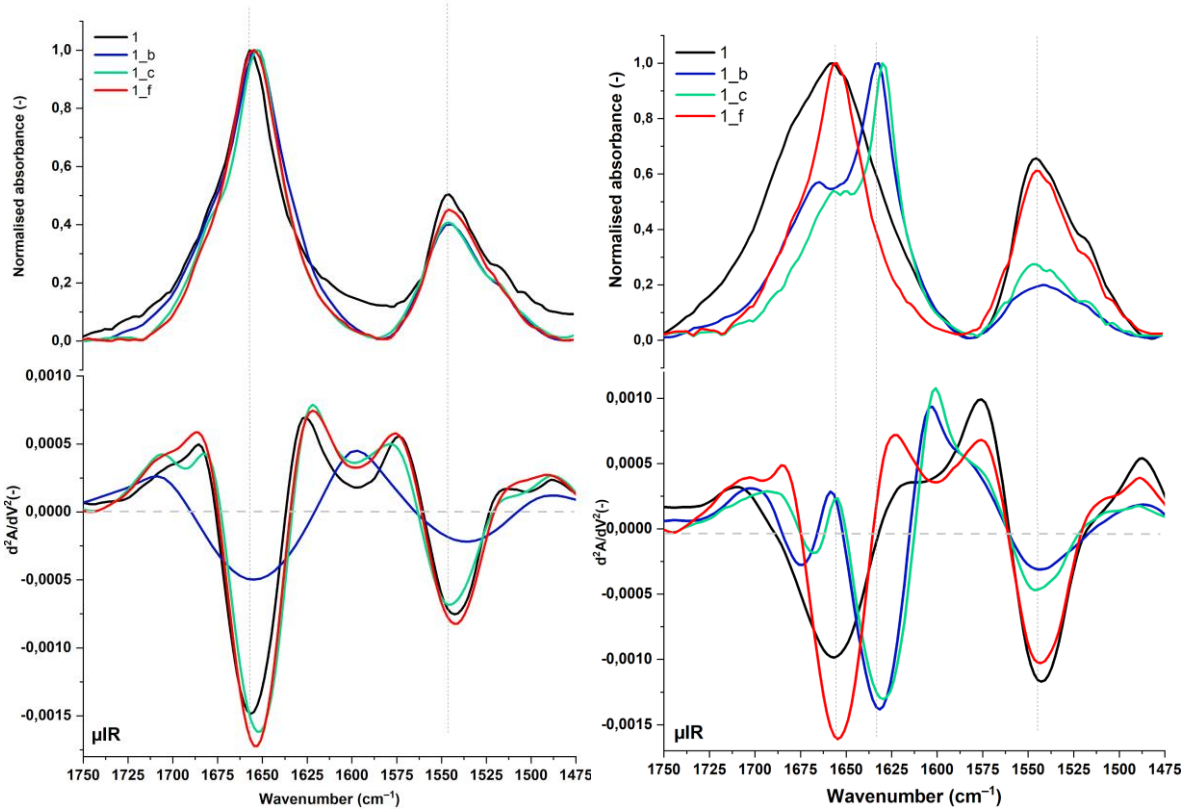

Figure S7_10. (left) Normalized µIR spectra of dissolved peptides in amide I and II range (1750 – 1475 cm^{-1}) with second derivatives. (right) Normalized µIR spectra of peptides in amide I and II range (1750 – 1475 cm^{-1}) with second derivatives after 7 days of incubation.

Table S7_11. Amide band positions in μIR spectra of 1.3 mM peptides solutions before and after 7 days of incubation.

1		**1_b**		**1_c**		**1_f**		**Assignment**
band position [cm^{-1}]								
0 days	**7 days**	0 days	**7 days**	0 days	**7 days**	0 days	**7 days**	
3300	3292	3298	3298	3299	3296	3295	3277	Amide A
3062	3067	3062	3063	3059	3058	3060	3075	Amide B
1655	**1655**	**1656**	**1657**	**1654**	**1654**	**1653**	**1630**	**Amide I**
1545	1545	1544	1547	1545	1543	1545	1543	Amide II

Table S6_12. Total percentage of peaks area attributed to aggregates and based on the decomposition of amide I (1700 – 1600 cm^{-1}) in μIR spectra of 1.3 mM peptides solutions before and after 7 days of incubation. The values were calculated as integrated absorbance of subbands in the range of 1635 – 1620 cm^{-1} and describe the content of the supramolecular-assemblies structures in the general conformation of each peptide.

1		**1_b**		**1_c**		**1_f**	
supramolecular-assemblies		**supramolecular-assemblies**		**supramolecular-assemblies**		**supramolecular-assemblies**	
0 days	**7 days**	0 days	**7 days**	0 days	**7 days**	0 days	**7 days**
3.2	6.85	0	19.74	0	29.95	5.44	03.01

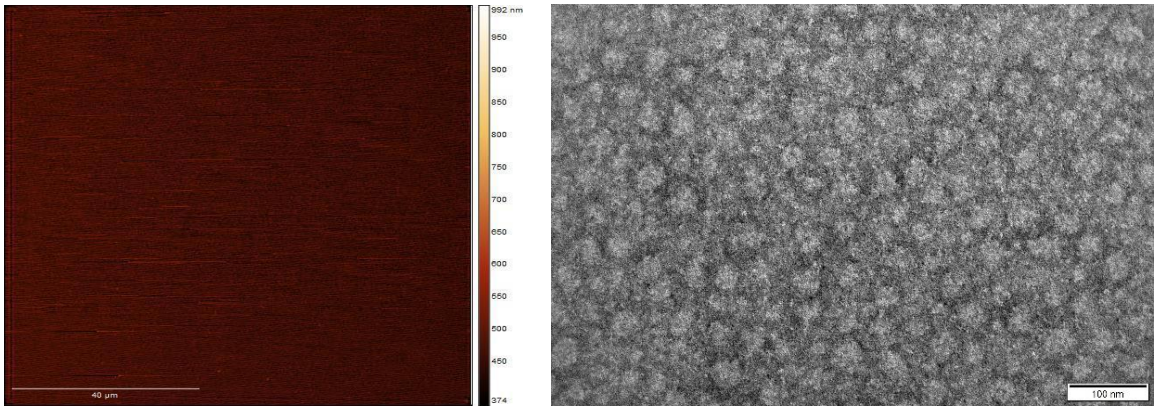

Figure S8_1. AFM (left) and TEM (right) images of 1mg/ml peptide **1** deposited on mica surface after 2 weeks of incubation at 37 ºC.

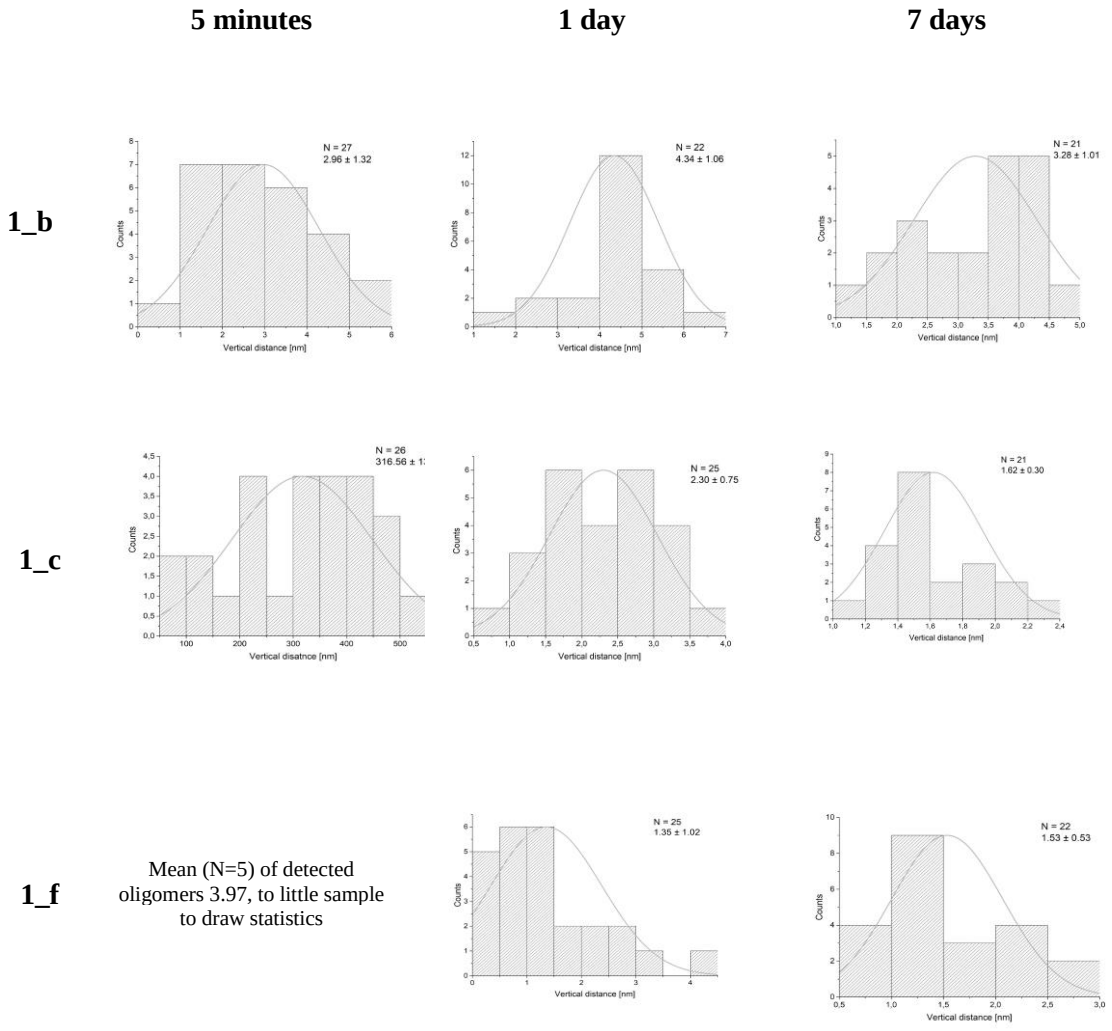

Figure S8_2. Height analysis of peptides nanostructures observed by AFM.

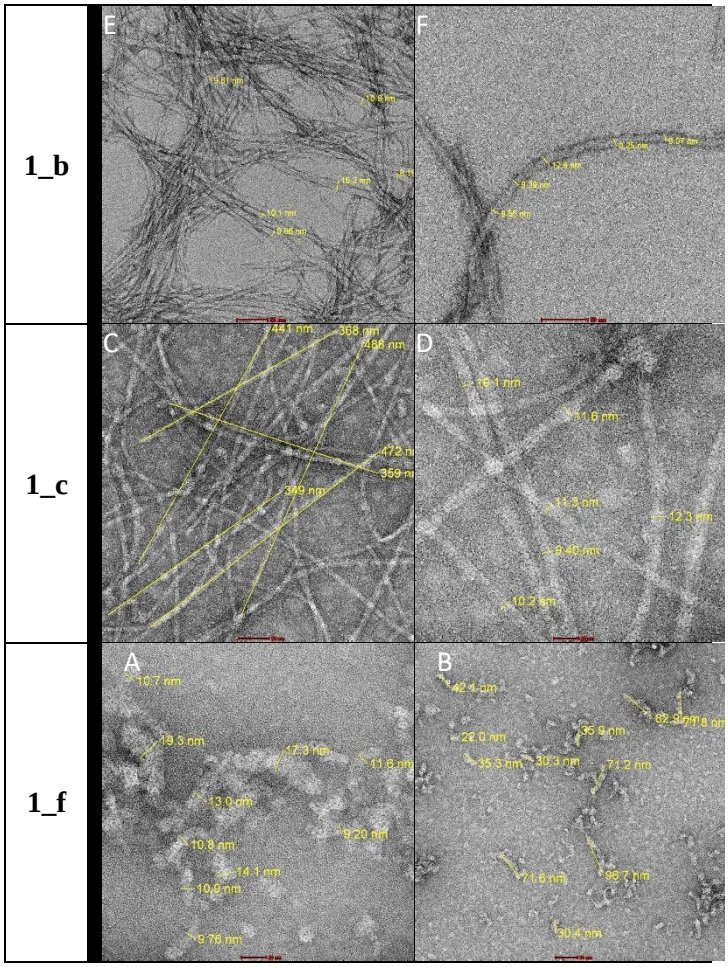

Figure S9. TEM images with marked fibrils dimensions.

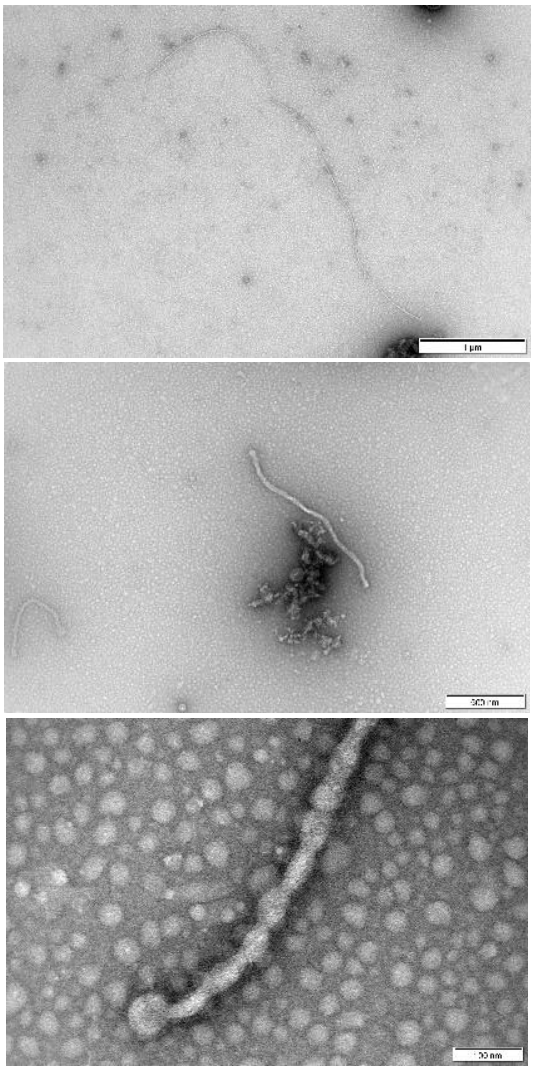

Figure S10. TEM images of peptide **1_f** after 7 days of incubation ($c_{peptide}$ = 1.3 mM).