Electronic Supplementary Information

Tuning self-assembly in elastin-derived peptides

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Materials of chemical synthesis of peptides.

Fmoc-amino acids were obtained from Inbios (Pozzuoli, Naples, Italy). Peptides were synthesized on solid support starting from Wang resin (Novabiochem, Darmstadt, Germany), 100-200 mesh, and amino acids were coupled using Fmoc–based peptide synthesis methods and commercially available Fmoc-protected amino acids.

General Peptide Synthesis

Swelling of the Wang-resin [4-(Hydroxymethyl)phenoxymethyl]polystyrene]. The Wang-resin (theoretical loading = 0.65 mmol/g, 0.25 mmol,0.365g) was suspended in 1,2-dichloromethane (20 mL) in a glass fritter disc sealed in glass column equipped with a faucet. The suspension was stirred for 30 minutes by an orbital shaker (speed 250 rpm).

Loading of the first amino acid. A solution of the first Fmoc–amino acid (1.25 mmol), DIC (6 mmol, 1.00 mL) in dry DMF (10 mL, 10:1 v/v), previously shaken for 30 minutes, was added to the column after the draining of DCM. DMAP (15 mg) was solubilized in DMF (500 microliters) and added to the suspension and the reaction mixture left under stirring at room temperature for 2 hours. The resin was drained, washed with DMF (3x20 mL), DCM (3x20 mL) and MeOH (3x20 ml). The resin was dried before determination of the loading. The loading procedure was repeated when the loading of the resin was found to be < 80%.

Stepwise Elongation. Fmoc-Gly-Wang-resin (Loading of the resin was 0.52 mmol/g, 50 μmol, 100 mg) was submitted to fourteen cycles of Fmoc solid-phase synthesis with the appropriate commercial amino acid building blocks. The chemistry used was Fmoc–AA/HOBT/HBTU/DIPEA in 5/5/10 ratio on a Tribute® (Protein Technologies Inc.) automatic synthetizer.

Cleavage from the resin: After the final Fmoc deprotection, carried out by SPPS, the resin was treated with 95 % TFA in H_2O (1 mL) and left under stirring at room temperature for two hours.

HRMS experiments were performed by direct infusion into the electrospray ionization (ESI) source, coupled with a linear quadrupole ion trap mass spectrometer (Thermo Fisher Scientific, Bremen Germany). Positive ion ESI-MS was chosen for the detection:

$(LGGVG)_3$. HRMS (ESI): m/z 1169.67 $[M+H]^+$, 1168.3 calcd. for $[C_{51}H_{89}N_{15}O_{16}]^+$,1190.65 $[M+Na]^+$, 1206.63$[M+K]^+$

$(LGGLG)_3$. HRMS (ESI): m/z 1210.08$[M+H]^+$,1209.08 calcd. For $[C_{54}H_{95}N_{15}O_{16}]^+$,1248.05 $[M+K]^+$

$(VGGVG)_3$.HRMS (ESI): m/z 1126.61 $[M+H]^+$, 1125.61 calcd. For $[C_{48}H_{83}N_{15}O_{16}]^+$,1148.73 $[M+Na]^+$,1165.06 $[M+K]^+$

$(VGGLG)_3$.HRMS (ESI):m/z 1168.66 $[M+H]^+$, 1168.66 calcd. For $[C_{51}H_{89}N_{15}O_{16}]^+$, 1190.64$[M+Na]^+$, 1206.61 $[M+K]^+$

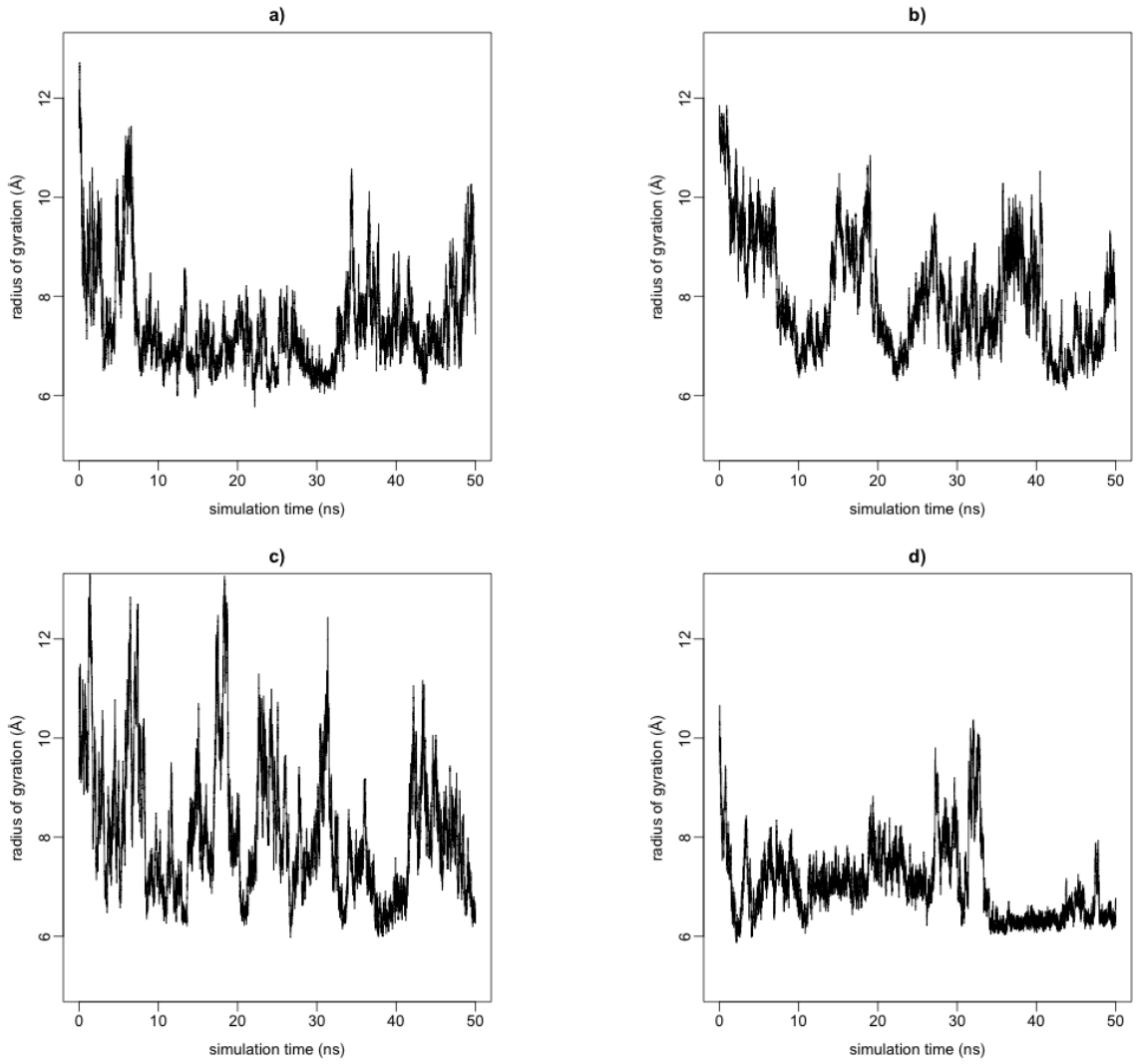

Figure S1: Radius of gyration generated from MD simulation measured along the trajectories for $(VGGVG)_3$ (a), $(VGGLG)_3$ (b), $(LGGVG)_3$ (c), $(LGGLG)_3$ (d).The radius of gyration fluctuates between 5.8 and 13.5 Å.

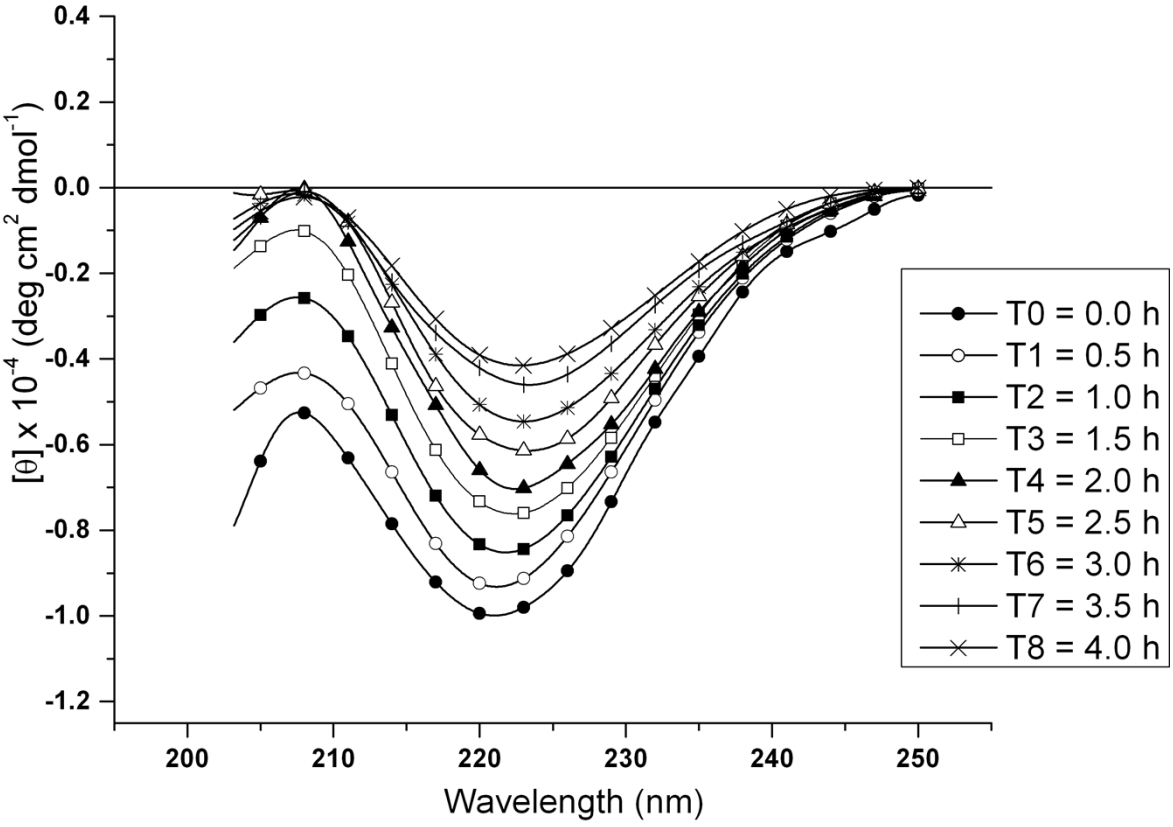

Figure S2. CD spectra of $(VGGVG)_3$ carried out in TBS at 310K as a function of time.

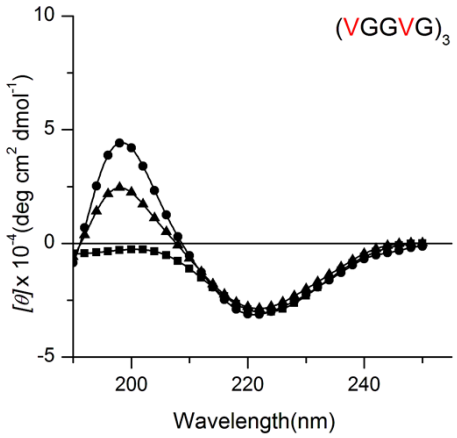

Figure S3. CD spectra of $(VGGVG)_3$ carried out in TFE-d_3/H_2O (80/20, v/v) at 273 (circles), 298 (triangles) and 343 K (squares).

Table S1: Assignments of proton resonances of peptide $(VGGLG)_3$ in TFE-d_3/H_2O (80/20, v/v) at 298 K

residue[a]	Chemical shift (ppm) NH	H_α	H_β	others	$^3J_{NH-H\alpha}$ (Hz)	-⊗™/⊗T (ppb/K)
V^1	-	3.83	2.24	1.07	-	-
G^2	8.40	4.16/3.88				6.1
G^3	8.04	4.00				5.6
L^4	7.77	4.46	1.66	1.67 0.95/0.92	7.5	5.0
G^5	8.09	4.07/3.90				5.6
$V^{1'}$	7.65	4.13	2.13	1.00	7.9	5.9
$G^{2'}$	8.16	4.01/3.91				7.0
$G^{3'}$	7.95	3.98				5.0
$L^{4'}$	7.75	4.41	1.66	1.67 0.95/0.92	7.5	5.7
$G^{5'}$	8.09	4.05/3.93				5.6
$V^{1''}$	7.63	4.20	2.13	0.99	8.2	5.3
$G^{2''}$	8.15	4.01/3.91				6.6
$G^{3''}$	7.93	3.98				5.0
$L^{4''}$	7.70	4.48	1.68	1.67 0.95/0.92	nd	5.0
$G^{5''}$	7.82	3.97				6.3

Table S2: Assignments of proton resonances of peptide $(LGGLG)_3$ in TFE-d_3/H_2O (80/20, v/v) at 298 K

	Chemical shift (ppm)					
residue[a]	NH	H_{α}	H_{β}	others	$^3J_{NH-H\alpha}$ (Hz)	-⊗™/⊗T (ppb/K)
L^1	-	4.05	1.77	1.77 0.99	-	-
G^2	8.42	4.16/3.87				6.3
G^3	8.04	4.03/3.96				5.9
L^4	7.75	4.45	1.68	1.68 0.99	7.5	5.9
G^5	8.08	4.04				5.8
$L^{1'}$	7.78	4.36	1.68	1.68 0.99	6.6	6.5
$G^{2'}$	8.15	4.00				5.9
$G^{3'}$	7.97	3.98				4.7
$L^{4'}$	7.74	4.39	1.70	1.70 0.99	7.0	5.9
$G^{5'}$	8.06	4.03				5.1
$L^{1''}$	7.72	4.39	1.74	1.70 0.97/0.92	7.0	5.5
$G^{2''}$	8.11	4.01				5.9
$G^{3''}$	7.95	3.98				5.0
$L^{4''}$	7.66	4.48	1.70	1.70 0.97/0.93	7.8	4.8
$G^{5''}$	7.81	3.97				5.5

Table S3: Assignments of proton resonances of peptide $(LGGVG)_3$ in TFE-d_3/H_2O (80/20, v/v) at 298 K

	Chemical shift (ppm)					
residue	NH	$H_{\langle}$	$H_{®}$	others	$^3J_{NH-H\langle}$ (Hz)	-⊗™/⊗T (ppb/K)
L^1	-	4.05	1.78	1.73 0.99	-	-
G^2	8.47	4.15/3.89				6.4
G^3	8.08	4.04/3.98				5.7
V^4	7.69	4.22	2.12	0.98	8.6	5.1
G^5	8.17	4.06/3.90				6.4
$L^{1'}$	7.82	4.38	1.66	1.67 0.97/0.92	7.4	6.2
$G^{2'}$	8.19	4.00/3.91				6.8
$G^{3'}$	8.01	3.98				5.0
$V^{4'}$	7.64	4.18	2.15	0.98	8.2	4.4
$G^{5'}$	8.13	4.03/3.93				5.7
$L^{1''}$	7.78	4.39	1.66	1.67 0.97/0.92	7.3	5.7
$G^{2''}$	8.17	4.05				6.4
$G^{3''}$	8.00	3.99				5.0
$V^{4''}$	7.59	4.24	2.16	0.98	8.8	4.4
$G^{5''}$	7.94	3.99				6.2

Table S4: Assignments of proton resonances of peptide $(VGGVG)_3$ in TFE-d_3/H_2O (80/20, v/v) at 298 K

residue	Chemical shift (ppm)				$^3J_{NH-H\langle}$ (Hz)	-⊗™/⊗T (ppb/K)
	NH	$H_\langle$	$H_®$	others		
V^1	-	3.83	2.24	1.07	0.0	-
G^2	8.40	4.16/3.88				6.3
G^3	8.04	4.03/3.96				5.7
V^4	7.64	4.21	2.14	0.98	8.7	4.7
G^5	8.13	4.08/3.910				0.0
$V^{1'}$	7.67	4.03	2.13	0.98	8.5	6.0
$G^{2'}$	8.16	4.03/3.91				nd
$G^{3'}$	7.96	4.02/3.95				5.0
$V^{4'}$	7.64	4.18	2.14	0.98	8.7	4.7
$G^{5'}$	8.10	4.05/3.93				5.7
$V^{1''}$	7.67	4.13	2.13	0.98	8.5	6.0
$G^{2''}$	8.17	4.02/3.92				nd
$G^{3''}$	7.96	4.01/3.95				5.0
$V^{4''}$	7.57	4.23	2.16	0.99	8.5	4.5
$G^{5''}$	7.88	3.98				6.4