Supporting Information for *ChemBioChem* F444

Solution structure and stability of tryptophan-containing nucleopeptide duplexes

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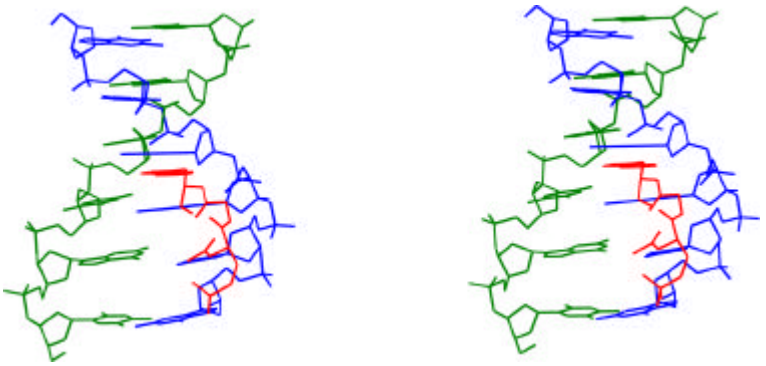

Figure S1: Stereoview of a model of [Ac-Lys-Trp-Lys-Hse($p^{3'}$dGCATCG)-Ala]-[$p^{5'}$dCGTAGC] (compound **I**), with the tryptophan intercalated between the central AT base-pairs. Blue: oligonucleotide chain of the nucleopeptide. Red: peptide chain. Green: complementary oligonucleotide strand.

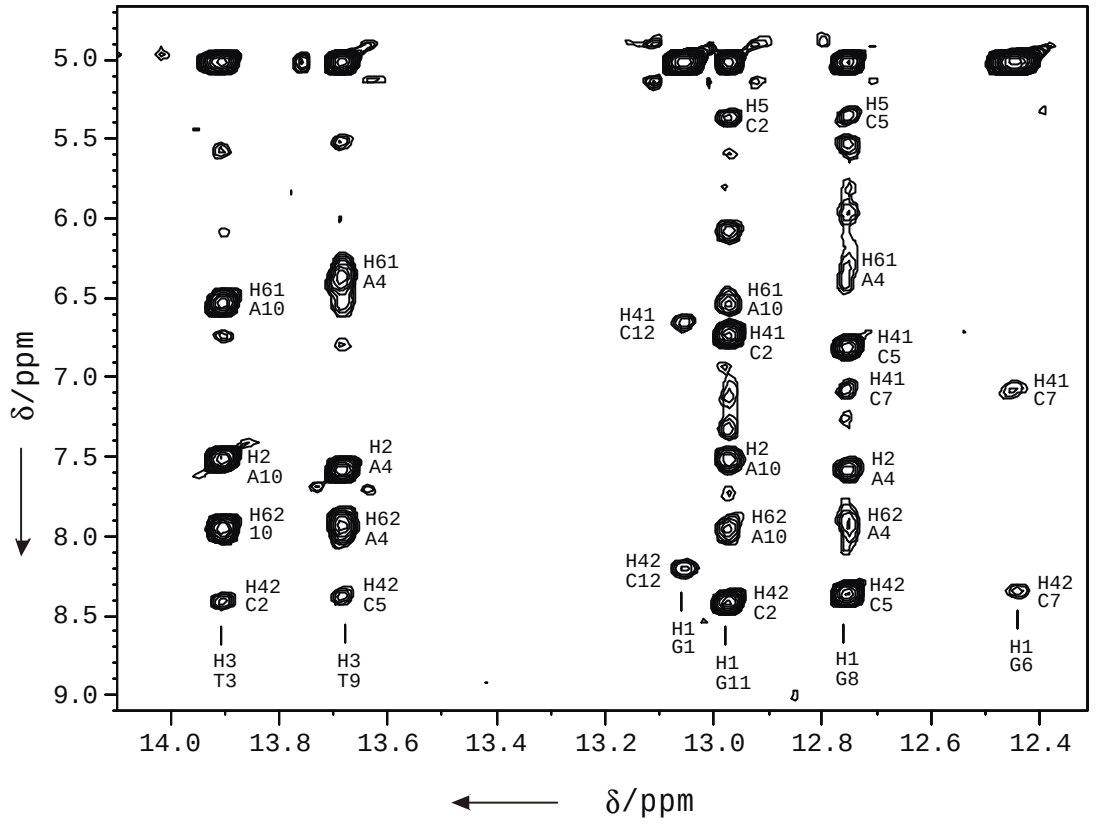

Figure S2. Imino region of the NOESY spectra of [Ac-Lys-Trp-Lys-Hse(p$^{3'}$dGCATCG)-Ala]-[p$^{5'}$dCGTAGC] in H_2O (100mM NaCl, T=5ºC, pH=7, τ_m= 200 ms).

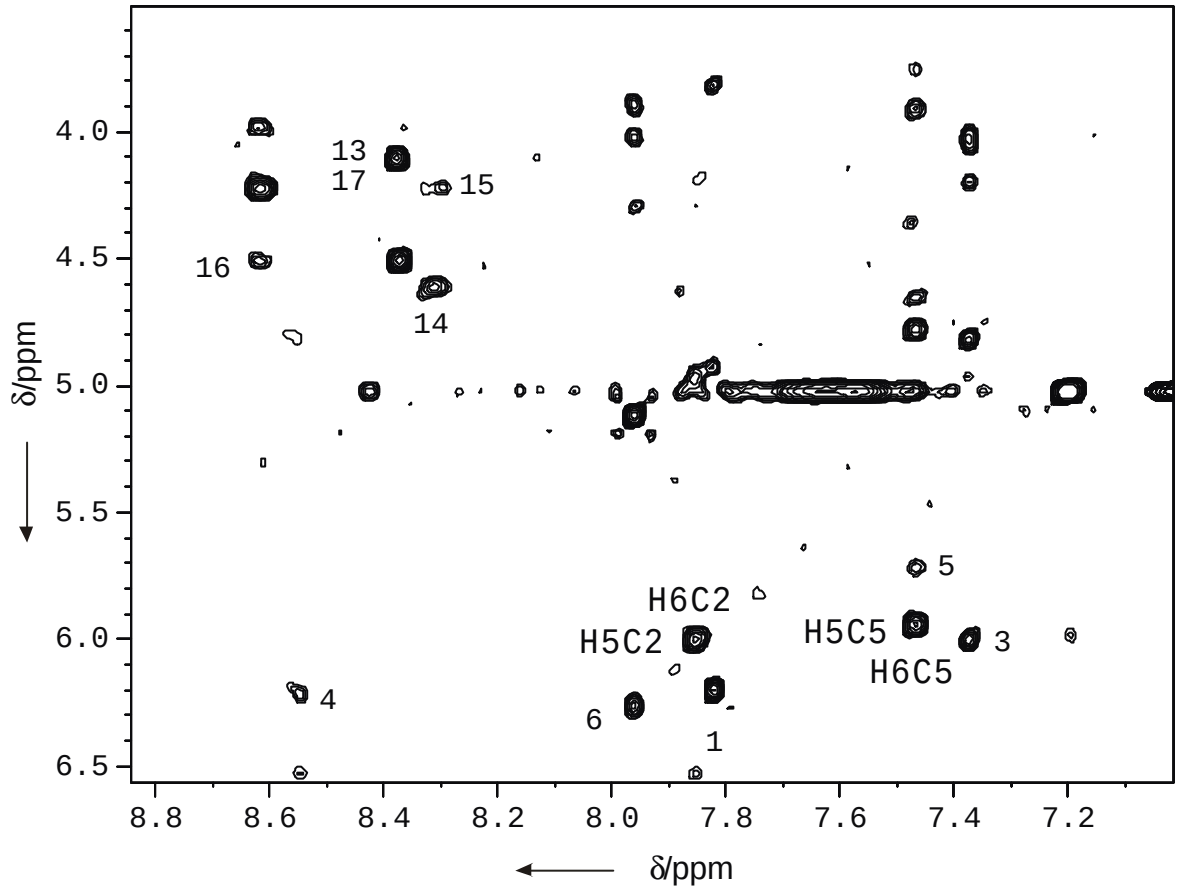

Figure S3. Fragment of the NOESY spectra of the single stranded form of [Ac-Lys-Trp-Lys-Hse($p^{3'}$dGCATCG)-Ala] in H2O (100mM NaCl, T=5ºC, pH=7, τ_m= 200 ms). Intra-residual Hα-HN, and H1'-H6/H8 are labelled with the residue number.

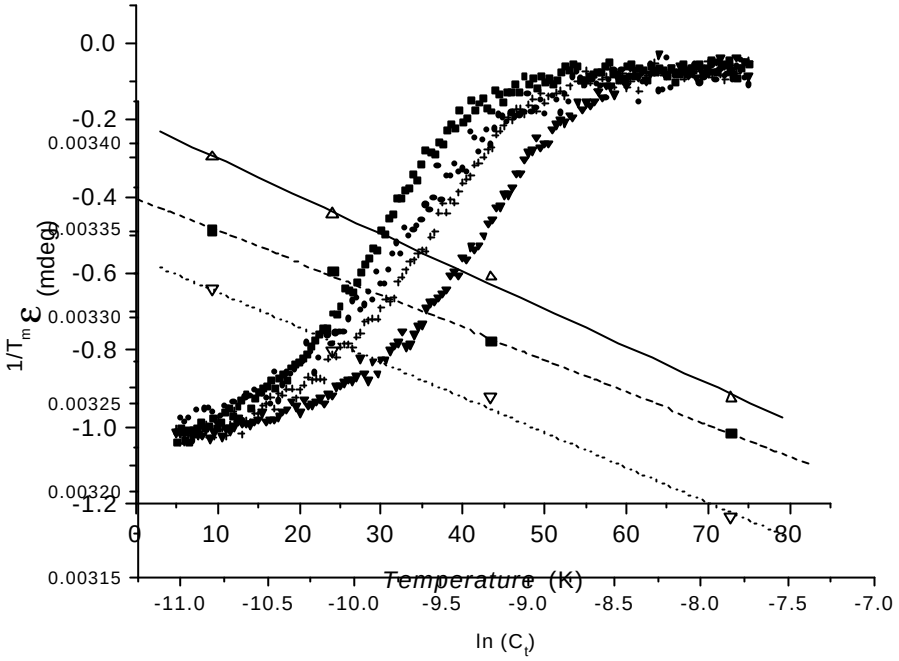

Figure S4: Top: CD melting curves of [Ac-Ala-Trp-Ala-HSE(p$^{3'}$GCATGC)-Ala]$_2$ at different concentrations (20 μM, 40 μM, 100 μM, and 400 μM). Bottom: Plot of 1/Tm versus lnC for the melting transition of [Ac-Ala-Trp-Ala-HSE(p$^{3'}$GCATGC)-Ala]$_2$ (up triangle), [Ac-Lys-Trp-Lys-HSE(p$^{3'}$GCATCG)-Ala]$_2$ (black square), and d(GCATCG)$_2$ (down triangle).

Table S1. ^{1}H-NMR assignments of [Ac-Lys-Trp-Lys-Hse(p$^{3'}$dGCATCG)-Ala-OH]-[p$^{5'}$dCGTAGC] (100mM NaCl, T=5ºC, pH=7).

Residue	H4'	H1'	H6/H8	H2'	H2"	H3'	H5'	H2/H5/M	$NH_2(2)$	$NH_2(1)$	NH
1GUA	4.30	6.01	8.01	2.71	2.80	4.87	3.76				13.06
2CYT	4.27	6.09	7.57	2.53	2.17	4.86		5.36	8.41	6.74	
3THY	4.16	5.59	7.49	2.22	2.48	4.91		1.70			13.91
4ADE	4.46	6.22	8.38	2.76	2.87	5.07	4.18	7.58	7.92	6.36	
5CYT	4.10	5.54	7.24	1.65	2.11	4.79	4.26	5.35	8.36	6.81	
6GUA	4.33	5.91	7.93	2.76	2.56	5.04	4.10				12.46
7CYT	4.14	5.79	7.73	2.13	2.49	4.78	3.78	5.97	8.34	7.09	
8GUA	4.19	6.00	8.05	2.73	2.81	4.86					12.76
9THY	4.19	5.51	7.34	2.16	2.41	4.89		1.55			13.69
10ADE	4.44	6.09	8.25	2.78	2.94	5.08	4.16	7.51	7.95	6.53	
11GUA	4.38	5.80	7.72	2.48	2.66	4.98					12.98
12CYT	4.05	6.08	7.34	2.18	2.18	4.47	4.27	5.22	8.21	6.65	

	HN	HA	HB/2/3	Others
13LYS^{+}	8.24	3.96	1.49	HG 1.16, HD 1.50, HE 2.82
14TRP	7.87	4.40	2.75/2.80	HD1 6.73, HE3 6.95, HE1 9.77, HZ3 6.72, HZ2 7.06 HH2 6.86
15LYS	7.99	4.14	1.55/1.67	HG 1.18, HD 1.55, HE 2.89
16HSE	8.49	4.54	2.01/2.26	HG2 3.97, HG3 4.12
17ALA	8.38	4.09	1.36	

$^{+}$Acetyl terminal group = 1.82 ppm

Table S2. ^{1}H-NMR assignments of $^{5'}$d(GCTACG)•$^{5'}$d(CGTAGC) (100mM NaCl, T=5ºC, pH=7).

Residue	H4'	H1'	H6/H8	H2'	H2"	H3'	H5'	H2/H5/M	$NH_2(2)$	$NH_2(1)$	NH
1GUA	4.31	6.03	8.03	2.73	2.81	4.88	3.78				13.04
2CYT	4.28	6.10	7.59	2.56	2.19	4.87		5.38	8.41	6.76	
3THY	4.21	5.62	7.51	2.26	2.53	4.94	4.12	1.73			13.93
4ADE	4.49	6.11	8.42	2.80	2.92	5.09		7.60	7.95	6.41	
5CYT	4.19	5.63	7.35	1.88	2.31	4.83		5.42	8.41	6.89	
6GUA	4.21	6.16	7.95	2.65	2.39	4.70					12.88
7CYT	4.11	5.76	7.70	2.12	2.48	4.76	3.76	5.94	8.21	7.13	
8GUA		6.01	8.06	2.73	2.83	4.89					12.88
9THY	4.22	5.55	7.37	2.19	2.45	4.92		1.57			13.73
10ADE	4.47	6.12	8.27	2.80	2.95	5.09	4.05	7.49	7.95	6.53	
11GUA	4.40	5.81	7.75	2.51	2.68	5.00					12.98
12CYT	4.07	6.11	7.39	2.20	2.20	4.50		5.31	8.21	6.67	

Table S3. Melting temperatures for some protons of [Ac-Lys-Trp-Lys-Hse($p^{3'}$dGCATCG)-Ala-OH]-[$p^{5'}$dCGTAGC] (**I**), and the control duplex (**II**).

Residue	Proton	Tm(°C)
W14 (**I**)	HZ2	44
W14 (**I**)	HE3	44
W14 (**I**)	HH2	45
W14 (**I**)	HD1	42
W14 (**I**)	HZ3	45
T3 (**I**)	Met	46
T9 (**I**)	Met	48
T3 (**II**)	Met	37
T9 (**II**)	Met	44

Table S4. Relaxation times.

Residue	Proton	T1(s)	T2(ms)	τ_c (ns)
A4	H8	2.16	52.42	1.97
A10	H8	2.10	45.73	2.07
G8	H8	1.93	71.35	1.59
G1	H8	1.98	51.04	1.91
G6	H8	2.25	83.56	1.59
C7,G11	H6,H8	1.96	78.63	1.53
C2,A4	H6,H2	3.06	51.08	2.37
A10	H2	3.69	59.18	2.42
T3	H6	2.22	59.18	1.88
T9,C12	H6	2.01	31.03	2.47
C5	H6	2.19	49.08	2.05
W14	HZ2	3.33	99.83	1.77
W14	HE3	2.27	79.36	1.64
W14	HH2	2.84	86.35	1.76
W14	HD1,HZ3	2.44	132.68	1.31

Table S5. List of peptide-DNA distance constraints.

Constraint				UPPER	LOWER
6	GUA	H2″	14 TRP HZ3	3.69	3.19
6	GUA	H1′	14 TRP HE3	4.28	3.78
6	GUA	H2″	14 TRP HE3	4.25	3.75
6	GUA	H2′	16 HSE HA	4.16	3.62
6	GUA	H2″	16 HSE HA	3.67	3.17
6	GUA	H1′	16 HSE HG2	3.58	3.08
6	GUA	H1′	16 HSE HG3	4.00	1.80
6	GUA	H2′	16 HSE HG2	4.00	2.57
6	GUA	H2″	16 HSE HG2	4.00	2.50
6	GUA	H1′	14 TRP HZ3	3.50	2.50
6	GUA	H1′	14 TRP HH2	5.00	4.00
6	GUA	H8	14 TRP HZ3	5.50	4.00
6	GUA	H8	14 TRP HE3	5.00	4.00
6	GUA	H1′	16 HSE HA	5.00	4.16
7	CYT	H1′	14 TRP HD1	5.00	1.80
7	CYT	H1′	14 TRP HE1	5.00	1.80
6	GUA	H1′	14 TRP HE1	5.50	1.80
6	GUA	H8	16 HSE HA	4.51	3.76