

Supporting Information

Disorder-to-Order Markers of a Cyclic Hexapeptide Inspired from the Binding Site of Fertilin β Involved in Fertilization Process

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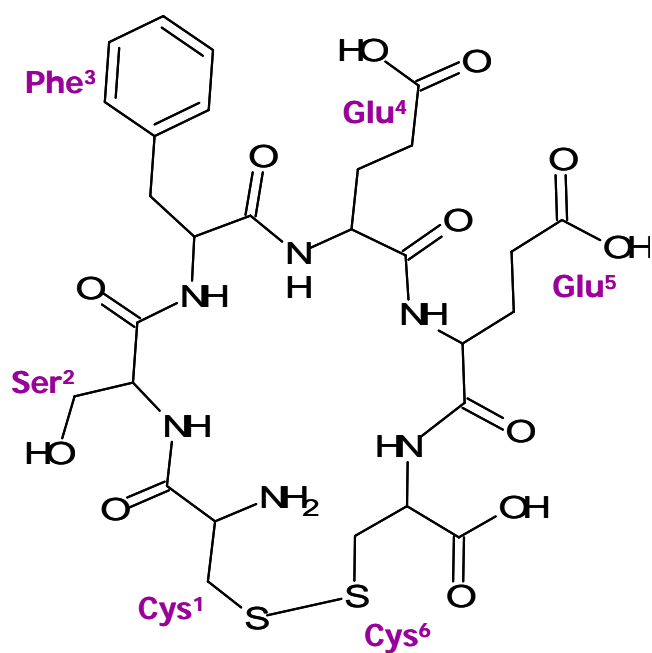
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Scheme 1 Amino acid composition of the cyclic hexapeptide cFEE. Residues are numbered from N^{ter} to C^{ter}. Cyclic structure is maintained by the Cys¹-Cys⁶ disulfide linkage.

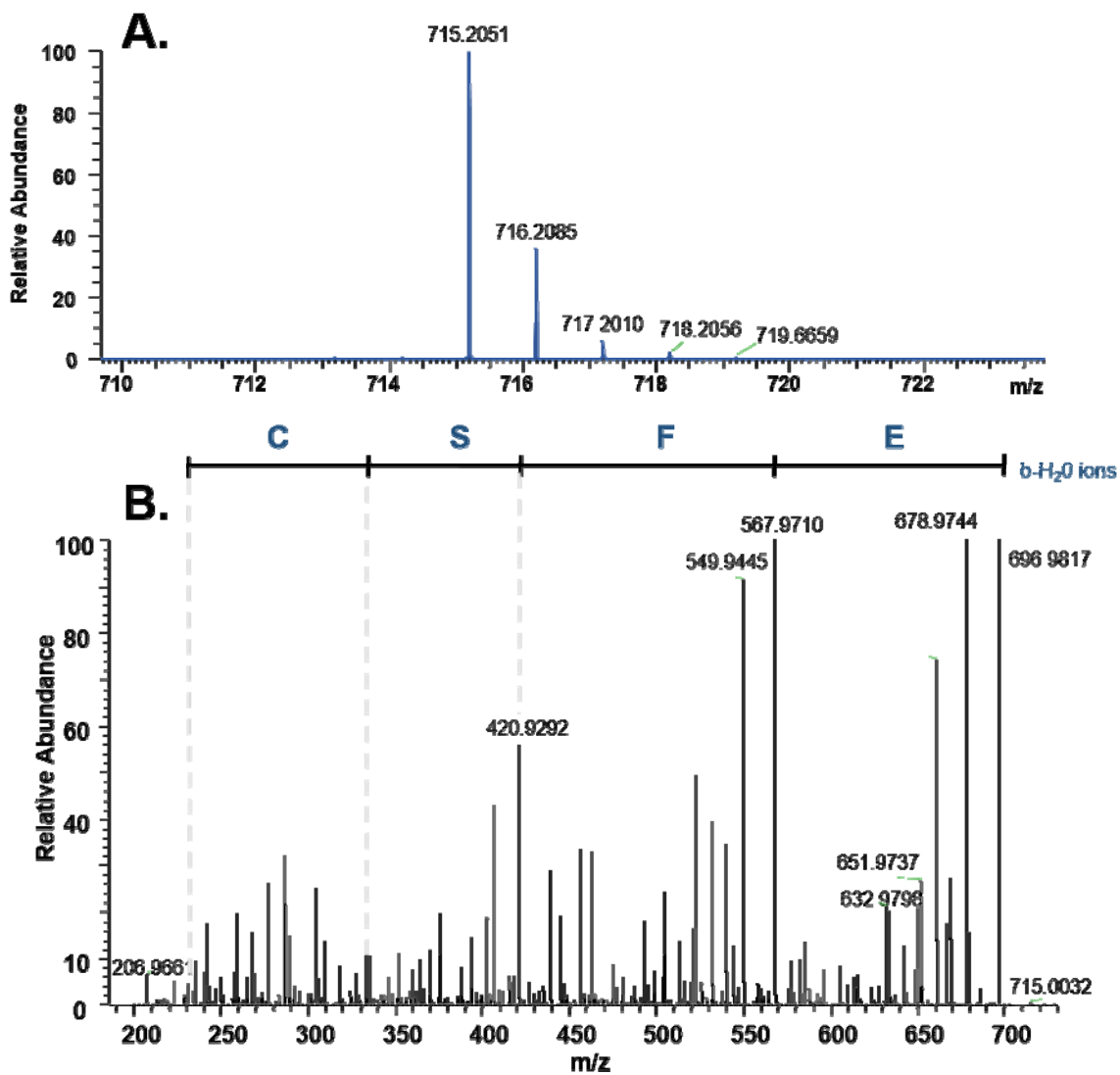


Figure S1 **A.** Example of mass spectrum obtained from LC-MS/MS analysis corresponding to the cFEE cyclic peptide (retention time 10.18 min; theoretical $m/z = 715.2062$). **B.** Raw MS/MS spectrum corresponding to the fragmentation of the cyclic peptide cFEE (precursor ion 715.20; charge state 1+).

Table S1. Observed and calculated modes of glutamate^a

Glu ¹⁻			Glu ⁰		
Obs ^b	Calc ^b	Assignment ^c	Obs ^b	Calc ^b	Assignment ^c
			1723	1712	$\nu(\text{C}\delta=\text{O})$; NtH ₃ ⁺ asymm. bend.
	1696	NtH ₃ ⁺ asymm. bend.		1689	NtH ₃ ⁺ asymm. bend.; $\nu(\text{C}\delta=\text{O})$
	1667	NtH ₃ ⁺ asymm. bend.; NtH ₃ ⁺ asymm. rock.		1662	NtH ₃ ⁺ asymm. bend. ; CtOO ⁻ asymm. st.
1602	1644	CtOO ⁻ asymm. st.	1602	1644	CtOO ⁻ asymm. st.
	1624	CtOO ⁻ asymm. st.		1627	CtOO ⁻ asymm. st.
	1566	C δ OO ⁻ asymm. st.; NtH ₃ ⁺ asymm. bend.		1501	NtH ₃ ⁺ symm. bend.; NtH ₃ ⁺ symm. rock.
	1519	NtH ₃ ⁺ symm. bend.; NtH ₃ ⁺ symm. Rock.; CtOO ⁻ asymm. st.			
1444	1472	C β H ₂ bend.	1450	1470	C β H ₂ bend.
	1457	C γ H ₂ bend.		1461	$\delta(\text{C}\delta-\text{O}-\text{H})$; C γ H ₂ bend.
	1414	C δ OO ⁻ symm. st.; C β H ₂ rock.; $\nu(\text{C}\gamma-\text{C}\delta)$		1447	C γ H ₂ bend.
1415	1411	CtOO ⁻ symm. st.; C β H ₂ rock.; $\delta(\text{O}-\text{Ct}-\text{O})$; $\delta(\text{Nt}-\text{C}\alpha-\text{H})$	1415	1411	C β H ₂ rock.; CtOO ⁻ symm. st.
				1395	Nt-C α -H; C β H ₂ rock.; $\delta(\text{C}\beta-\text{C}\alpha-\text{H})$
	1380	$\delta(\text{C}\beta-\text{C}\alpha-\text{H})$; $\delta(\text{Nt}-\text{C}\alpha-\text{H})$; C β H ₂ rock.		1387	C γ H ₂ rock.; $\delta(\text{C}\delta-\text{O}-\text{H})$; C β H ₂ twist.
1348	1361	CtOO ⁻ symm. st.; C β H ₂ rock.; $\delta(\text{Nt}-\text{C}\alpha-\text{H})$	1354	1365	CtOO ⁻ symm. st.; C β H ₂ rock.
1329	1348	C γ H ₂ rock.; C β H ₂ twist.; C δ OO ⁻ symm. st.	1325	1320	$\delta(\text{Ct}-\text{C}\alpha-\text{H})$; C β H ₂ twist.; CtOO ⁻ symm. st.
	1312	$\delta(\text{Nt}-\text{C}\alpha-\text{Ct})$; $\delta(\text{C}\beta-\text{C}\alpha-\text{H})$; C γ H ₂ rock.	1292	1304	C β H ₂ twist.; C γ H ₂ twist.; $\delta(\text{Ct}-\text{C}\alpha-\text{H})$
1288	1286	C β H ₂ twist.; C γ H ₂ twist.			
	1213	NtH ₃ ⁺ asymm. rock.; $\delta(\text{Nt}-\text{C}\alpha-\text{H})$		1238	$\nu(\text{C}\delta-\text{O})$; C γ H ₂ rock.
				1208	C γ H ₂ twist.
	1197	C γ H ₂ twist.; $\delta(\text{C}\beta-\text{C}\alpha-\text{H})$		1186	NtH ₃ ⁺ asymm. rock.; $\delta(\text{C}\beta-\text{C}\alpha-\text{H})$
	1166	NtH ₃ ⁺ asymm. rock.; $\delta(\text{Nt}-\text{C}\alpha-\text{H})$		1156	$\delta(\text{Ct}-\text{C}\alpha-\text{H})$; NtH ₃ ⁺ asymm. rock.
1081	1106	C β H ₂ wagg.; $\nu(\text{C}\beta-\text{C}\gamma)$	1082	1108	$\nu(\text{C}\beta-\text{C}\gamma)$; $\nu(\text{C}\alpha-\text{C}\beta)$; $\nu(\text{Nt}-\text{C}\alpha)$
1040	1025	$\nu(\text{Nt}-\text{C}\alpha)$; $\delta(\text{C}\alpha-\text{Ct}-\text{O})$; $\nu(\text{C}\beta-\text{C}\gamma)$			
1003	1016	C β H ₂ wagg.; C γ H ₂ wagg.; $\tau(\text{C}\beta-\text{C}\gamma)$; C β H ₂ scissor.	1003	1017	$\nu(\text{Nt}-\text{C}\alpha)$; $\nu(\text{C}\beta-\text{C}\gamma)$; C β H ₂ wagg.
	937	C γ H ₂ wagg.; C β H ₂ wagg.; C γ H ₂ scissor.		1016	C γ H ₂ wagg.; $\tau(\text{C}\beta-\text{C}\gamma)$; $\nu(\text{C}\alpha-\text{C}\beta)$
			919	922	C γ H ₂ wagg.; C β H ₂ wagg.; $\nu(\text{Nt}-\text{C}\alpha)$
883	916	$\nu(\text{C}\gamma-\text{C}\delta)$; $\delta(\text{OCtO})$		906	$\nu(\text{Ct}-\text{C}\alpha)$; $\nu(\text{C}\gamma-\text{C}\delta)$; C γ H ₂ wagg.
860	868	$\delta(\text{O}-\text{Ct}-\text{O})$; $\delta(\text{C}\alpha-\text{Ct}-\text{O})$; $\nu(\text{C}\alpha-\text{Ct})$	860	863	$\delta(\text{Ct}-\text{C}\alpha-\text{C}\beta)$; $\nu(\text{Ct}-\text{C}\alpha)$; $\delta(\text{O}-\text{Ct}-\text{O})$
				809	$\delta(\text{Ct}-\text{C}\alpha-\text{C}\beta)$
779	790	$\delta(\text{O}-\text{Ct}-\text{O})$; $\delta(\text{C}\alpha-\text{Ct}-\text{O})$	775	781	$\delta(\text{O}-\text{Ct}-\text{O})$; $\nu(\text{C}\alpha-\text{C}\beta)$; $\nu(\text{Nt}-\text{C}\alpha)$

^aWavenumbers are in cm⁻¹. No scaling factor was used to correct the calculated wavenumbers.^bObserved data are from the Raman spectra displayed in Figure 3C (Glu¹⁻) and Figure 3D (Glu⁰) (see main text). Calculated data are those obtained from the lowest energy conformers of the amino acid (see main text for details).^cAssignments are obtained on the basis of potential energy distribution (PED), as expressed in terms of internal coordinates.asymm. bend. Asymmetric bending coordinate; ν and δ refer to bond-stretch and angular bending vibrational motions; CH₂ angular bending vibrations are assigned by using the local symmetrical coordinates (twisting, wagging, rocking).

Table S2. Atomic Cartesian coordinates of cFEE as geometry optimized at the B3LYP/6-31G(d) level in a polarizable continuum mimicking methanol ($\epsilon_r=32.63$).

(L) cFEE with a left-handed disulfide bridge (see Figure 6A, main text, for graphical representation).

(R) cFEE with a right-handed disulfide bridge (see Figure 6B, main text, for graphical representation).

L			R				
	x	y	z	x	y	z	
C	-0.0890971707	0.0721059893	0.6070708592	C	0.0950239271	0.4712144737	0.4460162177
C	-0.5822386226	-0.1263715580	2.0507535925	C	-0.1842577304	0.4170110444	1.9572921353
O	0.0288786749	-0.8316019006	2.8673816612	O	0.7059445194	0.2222426070	2.7857004819
C	0.9444981825	-0.9926627986	0.2216572114	C	0.5761661822	-0.9283632978	0.0196856558
S	0.34896721300	-2.7453332620	0.2275902106	H	-0.8482365014	0.6821500787	-0.0743709232
H	-0.9616159209	0.0000812239	-0.0490432722	H	1.6127437683	-1.0727839058	0.3330825887
H	1.3513071846	-0.7789699125	-0.7700349475	H	-0.0386243711	-1.7093280205	0.4729341246
H	1.7682118993	-0.9932488508	0.9427078469	N	-1.4996115979	0.5487961235	2.2844581589
N	-1.7085812442	0.5485114855	2.3757995465	C	-1.9706012455	0.3793079624	3.6531276408
C	-2.2577724713	0.5100133849	3.7276033300	C	-3.0055360947	-0.7529984904	3.6736267444
C	-3.2197756842	-0.6855893994	3.869492996	O	-4.2087650009	-0.5224067561	3.4743535399
O	-4.4466341697	-0.535297884	3.9559089251	C	-2.5558597415	1.6738885066	4.2481031543
C	-2.9384228087	1.8336768624	4.0913774427	H	-2.1901039197	0.7134787408	1.5530534696
H	-2.2679703907	0.9795332191	1.6435145038	H	-1.0927191264	0.1014823907	4.2431208172
H	-1.4133620456	0.3549222403	4.4070636912	H	-2.8341055252	1.4786533871	5.2954669313
H	-3.2925343439	1.7678114509	5.1292846388	H	-1.7647401185	2.4302009695	4.2483804053
H	-2.1889168773	2.6294852158	4.0400044428	N	-2.5427889964	-2.0005530591	3.8852769579
N	-2.6164254968	-1.8941716120	3.8693382134	C	-3.4228802429	-3.1732282403	3.9357905365
C	-3.3409720557	-3.1689087405	3.9126863273	C	-4.2735220527	-3.2277388731	2.6419270137
C	-4.2624613427	-3.2974339094	2.6756935378	O	-3.7126963385	-3.3284185742	1.5487938907
O	-3.7794817048	-3.5964866158	1.5800578445	H	-1.5573447462	-2.1360703431	4.0667653413
H	-1.6078764582	-1.9075315021	3.7355853645	N	-5.6214185537	-3.1839582607	2.7614146742
N	-5.5887396639	-3.0784916497	2.8386707288	C	-6.4787930488	-3.2910445788	1.5912489136
C	-6.5070525145	-3.2347698082	1.7222097390	C	-6.2948075877	-2.1519494964	0.5704075813
C	-6.2760036922	-2.2121461298	0.5941482026	O	-6.6052074882	-2.3488998126	-0.6106484998
O	-6.5184459210	-2.5243810617	-0.5772565674	C	-7.9703987872	-3.3524582742	1.9798755054
C	-7.9806481480	-3.1559798373	2.1687758035	H	-6.0733010009	-3.0553678121	3.6625257975
H	-5.9652724379	-2.7596501362	3.7264384103	H	-6.2147742753	-4.1998134893	1.0390786421
H	-6.3257690253	-4.2072343088	1.2530080956	H	-8.2542571112	-2.4250187009	2.4907354738
H	-8.1928665620	-2.1635603163	2.5815987584	H	-8.5286932063	-3.3801344877	1.0400404545
H	-8.5824911033	-3.2549805321	1.2604664890	N	-5.8780706443	-0.9461854602	1.0339685456
N	-5.8863906311	-0.9617900476	0.9567155392	C	-5.6748660427	0.1631742042	0.0969370055
C	-5.6708896613	0.0700310958	-0.0642335861	C	-4.2854572279	0.0216928588	-0.5605688451
C	-4.2401793725	-0.0646039808	-0.6292006717	O	-3.2854258494	0.6203613990	-0.1478196079
O	-3.3064751418	0.6585967153	-0.2717241348	H	-5.4321643569	-0.8884982839	1.9506238927
H	-5.5449203976	-0.8017363072	1.9025129926	H	-6.4325272694	0.0385973370	-0.6815722217
H	-6.3723988683	-0.1660120642	-0.8696589582	N	-4.2645722917	-0.8243999444	-1.6174282087
N	-4.1112261319	-1.0622309699	-1.5430075320	C	-3.0319929872	-1.2166408042	-2.2839597258
C	-2.8160706472	-1.4642248803	-2.0664300926	C	-2.3791908361	-2.3955437445	-1.5249575043
O	-2.3238710114	-2.5111579706	-4.2006502986	H	-5.0945115114	-1.3907772989	-1.7879682446
C	-2.3084885881	-2.7555041945	-1.4061779932	H	-2.3515978143	-0.3635399938	-2.2827541854
S	-0.4972733802	-3.0533096282	-1.6586847414	H	-2.3742249169	-2.1603143579	-0.4584452207
H	-4.9117505251	-1.6811585806	-1.6623237101	H	-2.9716990702	-3.3081235920	-1.654438831
H	-2.1347226887	-0.6376909929	-1.8403902247	C	-8.3896364828	-4.5685467309	2.8197615807
H	-2.4996386345	-2.7298760713	-0.3320988547	H	-9.4473633097	-4.7956629299	2.6480709003
H	-2.8261272494	-3.6232277827	-1.8236013271	H	-7.8426724911	-5.4710714474	2.5160819677
C	-8.4256804692	-4.2416919012	3.1592700074	C	-8.2104073802	-4.4027805001	4.3128447525
H	-9.5053161710	-4.4079435256	3.0720748585	O	-7.5790677704	-3.5158459920	4.8659740968
H	-7.9606499673	-5.2091265302	2.9293080188	C	-5.8462639501	1.5381350719	0.7472998362

C	-8.1465701532	-3.9261147006	4.6128790809	H	-5.0650772957	1.7101966169	1.4912211629
O	-7.4852610900	-2.9893151672	5.0304616406	H	-5.6936103536	2.2845858358	-0.0391481327
C	-5.9447256267	1.4896265180	0.4374885703	C	-7.2380677843	1.7531782477	1.3642296218
H	-5.2212117219	1.7707584323	1.2057745176	H	-7.4213274112	2.8319924169	1.4522759811
H	-5.7727049562	2.1627637124	-0.4086941738	H	-8.0297290375	1.3488191405	0.7274279174
C	-7.3798993044	1.6955759677	0.9407875504	C	-7.3792310202	1.2040198904	2.7670648875
H	-7.6089307966	2.7697956435	0.9364544100	O	-6.5491933630	1.3149225674	3.6505066113
H	-8.1151798227	1.2211657526	0.2839040965	O	-3.6398333778	2.2172120380	3.5163358263
C	-7.6102244400	1.2388935340	2.3640464346	H	-4.3843891548	1.5883931985	3.5849805426
O	-6.7907561989	1.2793010295	3.2642771303	H	-2.7608718191	-4.0404016667	3.857012686
O	-3.9849901984	2.1984653722	3.2085337415	C	-4.1905193431	-3.2640845413	5.275763662
H	-4.7397906741	1.6018404494	3.3795518501	H	-4.8550591830	-4.1338476731	5.2286209208
H	-2.5813149962	-3.9370639728	3.7492545547	H	-4.8196890900	-2.3758959110	5.3891717664
C	-4.0110629383	-3.4326386872	5.2824514995	C	-3.2656226850	-3.3970184143	6.4682274692
H	-4.5879330908	-4.3608043112	5.1946704911	C	-2.6977823420	-4.6379755860	6.7936273248
H	-4.7182704507	-2.6299316448	5.5069596292	C	-2.9444111175	-2.2866963556	7.2605299631
C	-3.0038695474	-3.5588267486	6.406462438	C	-1.8288425274	-4.7654567566	7.8784174313
C	-2.3060400791	-4.7589913448	6.6077844029	H	-2.9434593484	-5.5130508158	6.1954672793
C	-2.7341813861	-2.4787880852	7.2576696666	C	-2.0761165086	-2.4100868172	8.3480857277
C	-1.3614806757	-4.8761155143	7.6286962725	H	-3.3839925739	-1.3192317428	7.0296443549
H	-2.5086684327	-5.6113467096	5.9624225200	C	-1.5143492325	-3.6499387654	8.6593330394
C	-1.7904362424	-2.5916858577	8.2816015889	H	-1.4021182577	-5.7360781298	8.1169777607
H	-3.2729140468	-1.5440696015	7.1214302177	H	-1.8421561317	-1.5379066077	8.9527966357
C	-1.0999034394	-3.7908088825	8.4694617271	H	-0.8406699619	-3.7481168634	9.5062264553
H	-0.8340521893	-5.8157080645	7.7708274770	N	1.1469530444	1.4617256505	0.1723683933
H	-1.5978980733	-1.7435273673	8.9334134876	H	1.2906167150	1.5089131257	-0.8374292336
H	-0.3672950557	-3.8811659372	9.2669064473	H	0.8036966646	2.3874249568	0.4301738000
N	0.4178948247	1.4483579078	0.4784005871	C	-3.3835601870	-1.6048654684	-3.7156304453
H	1.2895603229	1.5431539199	1.0008747209	O	-4.4035500123	-2.1879175304	-4.0218279103
H	0.6543830915	1.6258036053	-0.4972090541	O	-8.8434772405	-5.3668254787	4.9999194109
C	-2.8422595215	-1.5985726327	-3.5901254158	H	-8.6754819134	-5.2131811112	5.9502887830
O	-8.7311360544	-4.8146800171	5.4333918300	O	-8.5714467226	0.6063456755	2.9719338923
H	-8.5049155102	-4.5638561412	6.3503102058	H	-8.5996456093	0.3296612622	3.9089650056
O	-8.8733220611	0.8135218485	2.5658425066	S	0.4628441053	-1.1564583813	-1.8217734667
H	-8.9595056032	0.5977054726	3.5153039140	S	-0.6827618624	-2.8882739339	-2.0444317544
O	-3.4759157704	-0.5735276872	-4.1826009470	O	-2.4290401574	-1.2515239211	-4.5880230756
H	-3.4238396756	-0.7173538522	-5.1478082089	H	-2.6980184955	-1.5733402413	-5.4715807605