

Supporting Information

CC2 Benchmark for models of phenylalanine protein chains: 0-0 transition energies and IR signatures of the $\pi\pi^*$ excited state.

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Appendix S1: Definition of the characteristic dihedral angles of the backbone of capped peptides.

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Appendix S11: DFT-D structures of the ground state of QFa A, B and C

References

Appendix S1: Definition of the characteristic dihedral angles of the backbone of capped peptides.

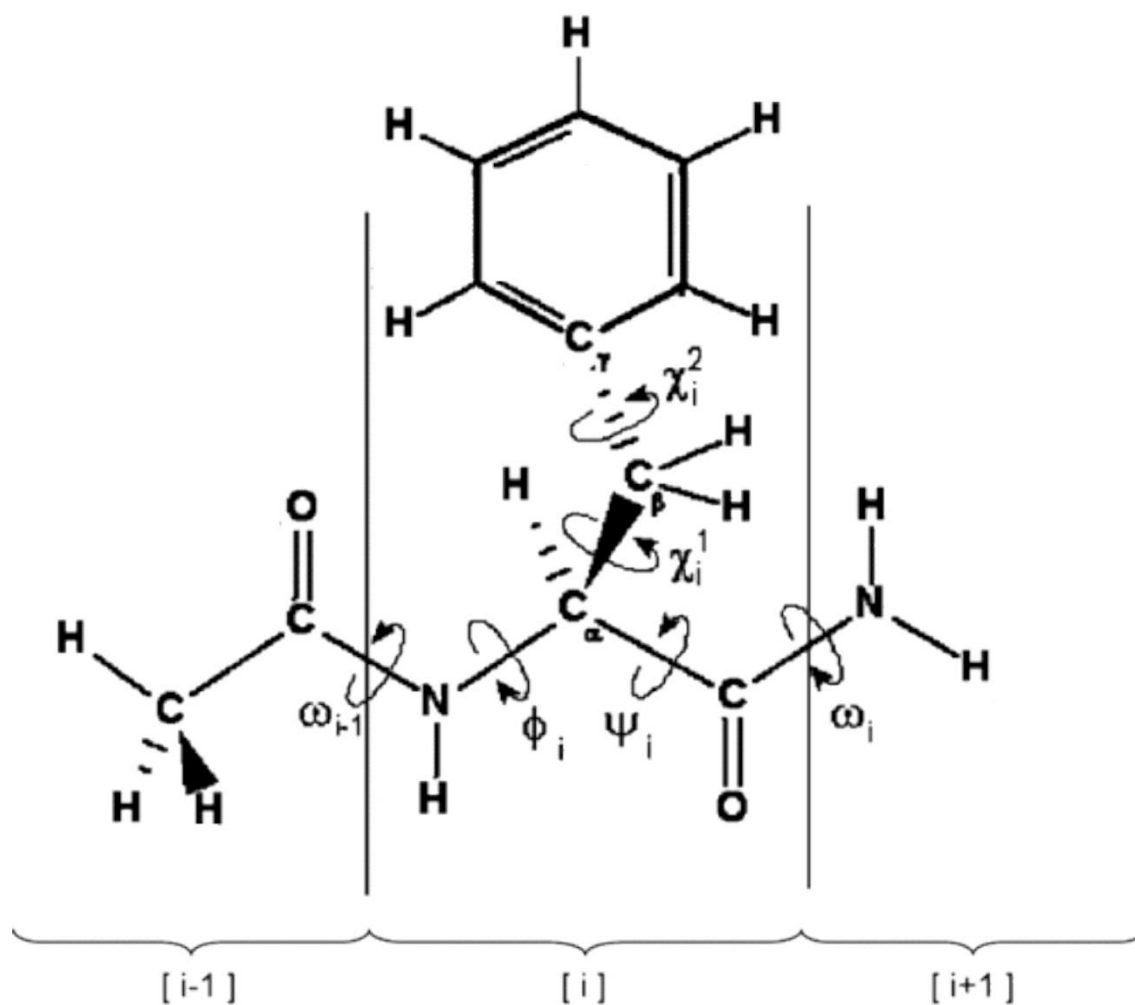


Figure S1: Definition of the characteristic dihedral angles of the backbone of capped peptides: Example of N-Ac-Phe-NH₂ (Fa) from the N-terminus (left-most [i-1] module) through the central Phe (central [i] module) to C-terminal NH₂ protecting group (right-most [i+1] module).

Appendix S2: Characteristic geometrical parameters of the DFT-D optimized geometry of the ground state (S_0) of the four Fa conformers.

		Dihedral angles ($^\circ$) ^a			Intermolecular distances (\AA)	
		Φ	Ψ	χ^1	$d_{\text{NH}\dots\text{O}}$	$d_{\text{NH}\dots\pi}$ ^b
S_0	A	-160	159	192	2.28	2.56 (3.37, 2.84)
	B	-83	55	44	2.02	2.44 (3.23, 2.54)
	C	-85	72	-55	2.03	2.77 (3.76, 2.85)
	D	-83	84	193	2.24	

Table S2: Characteristic geometrical parameters of the ground state (S_0) of the four Fa conformers optimized at the DFT-D level.¹⁻²

^a For the definition of the dihedral angles, see the Supporting Information (Figure S1).

^b The $\text{NH}\dots\pi$ bond is characterized by three distances: the distance of the NH_{Phe} (A conformer) or NH_2 (B conformer and C conformer) hydrogen atom with the C_γ carbon atom of the phenylalanine residue and given in parentheses by the two distances with the two C_δ carbon atoms ($\text{C}_\delta^{\text{C-term}}$, $\text{C}_\delta^{\text{N-term}}$) of the phenylalanine residue.

Appendix S3: Comparison of the CC2/cc-pVXZ (X=D and T) optimized geometries of both the S_0 and S_1 states for the four Fa conformers.

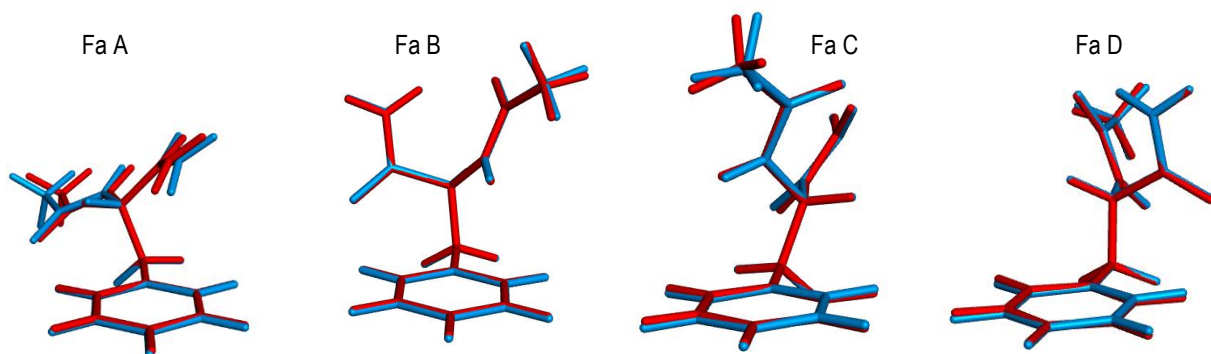


Figure S3-1: Comparison of the CC2/cc-pVDZ (blue) and CC2/cc-VTZ (red) optimized geometries of the S_0 state for the four Fa conformers. For each conformer, the phenyl rings have been overlapped.

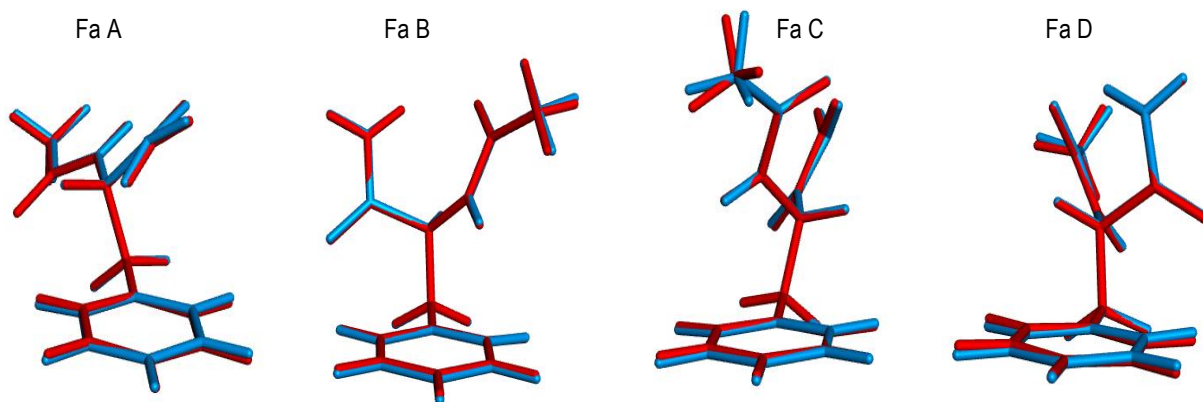


Figure S3-2: Comparison of the CC2/cc-pVDZ (blue) and CC2/cc-VTZ (red) optimized geometries of the S_1 state for the four Fa conformers. For each conformer, the phenyl rings have been overlapped.

Appendix S4: *Amide A* region frequencies of both the ground (S_0) and $\pi\pi^*$ excited (S_1) states of the four Fa conformers.

Conformer/State		NH _{phe}	NH _{2 sym.}	NH _{2 anti.}
cc-pVDZ				
Fa A	S_1	3594	3546	3695
	S_0	3583	3561	3713
Fa B	S_1	3545	3469	3689
	S_0	3589	3474	3690
Fa C	S_1	3553	3473	3674
	S_0	3597	3476	3675
Fa D	S_1	3618	3498	3677
	S_0	3618	3500	3677
Experiment				
Fa A	S_1	3434	3417	3535
	S_0	3433	3426	3541
Fa C	S_1	3439	3344	3514
	S_0	3463	3345	3515
cc-pVTZ				
Fa A	S_1	3590	3549	3698
	S_0	3588	3569	3712
Fa B	S_1	3524	3454	3686
	S_0	3577	3460	3687
Fa C	S_1	3560	3463.9	3688
	S_0	3614	3471	3683
Fa D	S_1	3627	3501	3682
	S_0	3627	3504	3681

Table S4: CC2/cc-pVXZ (X=D and T) *amide A* region frequencies (cm^{-1}) of both the ground (S_0) and $\pi\pi^*$ excited (S_1) states of the four Fa conformers, together with the available experimental ones.

Appendix S5: ZPVE of both the ground (S_0) and $\pi\pi^*$ excited (S_1) states according to the basis set for the four Fa conformers.

			ZPVE (au)
S_0	cc-pVDZ	A	0.238368
		B	0.239126
		C	0.238832
		D	0.239007
	cc-pVTZ	A	0.238510
		B	0.239284
		C	0.238696
		D	0.239019
S_1	cc-pVDZ	A	0.232277
		B	0.232950
		C	0.232845
		D	0.232960
	cc-pVTZ	A	0.232336
		B	0.233100
		C	0.232730
		D	0.232907

Table S5: ZPVE (au) of the optimized geometry of both the ground (S_0) and $\pi\pi^*$ excited (S_1) states obtained at the CC2/cc-pVXD (X=D and T) levels for the four Fa conformers. The values for S_0 state at the DFT-D/TZVPP level are 0.233370 (A), 0.233924 (B), 0.233337 (C) and 0.233567 (D).

Appendix S6: Comparison of the CC2/cc-pVDZ optimized geometry of the S_0 and S_1 states of Fa B and D.

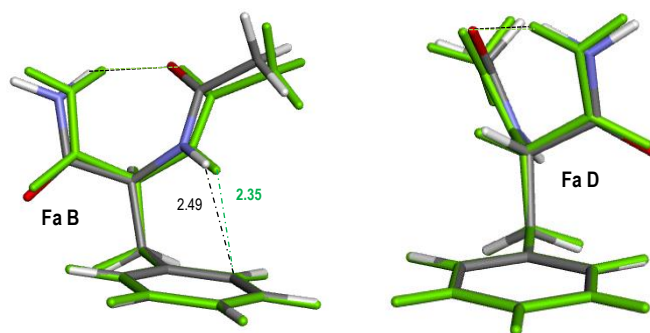


Figure S6: Comparison of the CC2/cc-pVDZ optimized geometries of the S_0 (atom-based colors) and S_1 (green) states for Fa B and D. For each conformer, the phenyl rings have been overlapped. Only distances (dash-dot) that vary significantly ($|d| > 0.01 \text{ \AA}$) between the ground and the excited state (see Table 1) are mentioned.

Appendix S7: Characteristic geometrical parameters of CC2/cc-pVDZ optimized geometry of both the ground (S_0) and lowest $\pi\pi^*$ excited (S_1) states of the Fm, GFA, FFa and QFa conformers.

Fm		Dihedral angles ($^\circ$) ^a			Intramolecular distances (\AA)	
		Φ	Ψ	χ^1	$d_{\text{NH}\dots\text{O}}$	$d_{\text{NH}\dots\pi}$ ^b
S_0	A	-163	152	183	2.22	2.59 (2.94, 2.80)
	B	-83	60	41	1.92	2.34 (2.50, 3.10)
	C	-89	75	-51	1.96	2.58 (3.48, 2.72)
S_1	A	-165	153	177	2.23	2.54 (3.02, 2.54)
	B	-84	60	43	1.92	2.35 (2.33, 3.28)
	C	-89	75	-50	1.96	2.52 (3.49, 2.53)

Table S7-1: Characteristic geometrical parameters of CC2/cc-pVDZ optimized geometry of both the ground (S_0) and lowest $\pi\pi^*$ excited (S_1) states of the Fm conformers.

^a For the definition of the dihedral angles, see the Supporting Information (Figure S1).

^b The $\text{NH}\dots\pi$ bond is characterized by three distances: the distance of the NH_{phe} (A conformer) or $\text{NH}_{\text{C-term}}$ (B and C conformer) hydrogen atom with the C_γ carbon atom of the phenyl residue and given in parentheses by the two distances with the two C_δ carbon atoms ($\text{C}_\delta^{\text{to C-term}}$, $\text{C}_\delta^{\text{to N-term}}$) of the phenyl residue.

GFA		Dihedral angles ($^\circ$) ^a			Dihedral angles ($^\circ$)			Intramolecular distances (\AA)	
		Φ_1	Ψ_1	χ_1^1	Φ_2	Ψ_2	χ_2^1	$d_{\text{NH}\dots\text{O}}$ ^b	$d_{\text{NH}\dots\pi}$ ^c
S_0	A	-81	67		-84	79	-59	1.96 - 1.99	2.87 (3.86, 3.03)
	A'	-279	295		-81	80	-57	1.92 - 1.99	
	B	-71	346		-91	9	53	1.92	2.45 (3.29, 2.48)
	B'	-304	220		-100	14	55	2.01	2.64 (3.47, 2.67)
	C	-115	166		-161	161	193	2.26 - 2.16	2.48 (2.67, 2.95)
S_1	A	-80	71		-86	78	-55	1.95 - 1.98	2.70 (3.54, 3.06)
	A'	-279	293		-80	80	-56	1.93 - 1.99	
	B	-70	345		-91	9	53	1.91	2.44 (3.33, 2.40)
	B'	-304	220		-95	10	57	2.01	2.60 (3.50, 2.56)
	C	-113	166		-165	155	181	2.28 - 2.21	2.52 (2.92, 2.63)

Table S7-2: Characteristic geometrical parameters of CC2/cc-pVDZ optimized geometry of both the ground (S_0) and lowest $\pi\pi^*$ excited (S_1) states of the GFA conformers.

^a For the definition of the dihedral angles, see the Supporting Information (Figure S1). The residue 1 correspond to the first residue from the N terminal cap, the N-term.

^b A and A' conformers: the two distances correspond to the two C_7 hydrogen bond distances. B and B' conformers, the distance is that of the C_{10} H-bond. C conformer: the two distances correspond to the two C_5 H-bond distances.

^c The $\text{NH}\dots\pi$ bond is characterized by three distances: the distance of NH_{phe} (B and B' conformer) or NH_2 (C conformer) hydrogen atom with the C_γ carbon atom of the phenylalanine residue and given in parentheses by the two distances with the two C_δ carbon atoms ($\text{C}_\delta^{\text{to C-term}}$, $\text{C}_\delta^{\text{to N-term}}$) of the phenylalanine residue.

FFa		Dihedral angles (°) ^a			Dihedral angles (°)			Intramolecular distances (Å)	
		Φ ₁	Ψ ₁	χ ₁ ¹	Φ ₂	Ψ ₂	χ ₂ ¹	d _{NH...O} ^b	d _{NH...π} ^c
S ₀	A	-69	353	62	-110	14	51	2.15	[2.62, 2.54] -[2.42, 2.41]
	B	-153	27	51	-95	75	-41	2.05	[2.70, 2.85] -[2.45, 3.00]
	C	-163	151	181	-80	70	45	1.99 - 2.24	2.60 (2.94, 2.74) - 2.49 (3.41, 2.50)
S ₁	A ₁	-68	349	61	-103	12	52	2.10	[2.59, 2.47] - [2.43, 2.41]
	A ₂	-69	352	62	-111	12	50	2.17	[2.63, 2.56] - [2.38, 2.33]
	B ₁	-151	24	52	-95	75	-40	2.03	[2.66, 2.78] - [2.43, 2.99]
	B ₂	-152	27	51	-95	75	-40	2.05	[2.68, 2.87] - [2.42, 2.94]
	C	-160	161	182	-73	67	41	1.96 - 2.21	2.46 (2.62, 3.15) - 2.24 (3.23, 2.17)

Table S7-3: Characteristic geometrical parameters of CC2/cc-pVDZ optimized geometry of both the ground (S₀) and lowest $\pi\pi^*$ excited (S₁) states of the FFa (Ac-Phe1-Phe2-NH₂) conformers.

^a For the definition of the dihedral angles, see the Supporting Information (Figure S1). The residue 1 correspond to the first residue from the N-term.

^b A, A₁ and A₂ conformers: the distance corresponds to the C₁₀ hydrogen bond distances. B, B₁ and B₂ conformers, the distance is that of the C₇ H-bond. C conformer: the distances correspond to the C₇ and the C₅ H-bond distances.

^c The NH... π bond is characterized by two group of distances. A and B conformers: the distances of the NH_{Phe1} hydrogen atom with the C _{γ} and the C _{$\delta^{\text{to N-term}}$} carbon atoms of Phe1 and those of the NH_{Phe2} hydrogen atom with the C _{γ} and the C _{$\delta^{\text{to N-term}}$} carbon atoms of Phe2. C conformer: the distances of the NH_{Phe2} hydrogen atom with the C _{γ} and the two C _{δ} carbon atoms (C _{$\delta^{\text{to C-term}}$} and C _{$\delta^{\text{to N-term}}$}) of Phe1 and those of the same hydrogen atom with the C _{γ} and the two C _{δ} carbon atoms (C _{$\delta^{\text{to C-term}}$} and C _{$\delta^{\text{to N-term}}$}) carbon atoms of Phe2.

QFa		Dihedral angles (°) ^a			Dihedral angles (°)			Intramolecular distances (Å)	
		Φ ₁	Ψ ₁	χ ₁ ¹	Φ ₂	Ψ ₂	χ ₂ ¹	d _{NH...O} ^b	d _{NH...π} ^c
S ₀	A	-74	349	-63	-93	10	53	1.82 - 2.00	2.33 (3.25, 2.47)
	B	-76	348	79	-106	13	-58	1.87 - 2.01	2.86 (2.63, 2.75)
	C	-69	343	71	-96	14	51	1.85 - 1.99	2.43 (3.19, 2.43)
S ₁	A	-65	340	-58	-106	15	47	1.83 - 2.06	2.37 (3.07, 2.35)
	B	-69	341	67	-112	16	-50	1.84 - 2.04	2.92 (2.81, 2.36)
	C	-69	342	69	-97	14	48	1.85 - 2.00	2.39 (3.11, 2.39)

Table S7-4: Characteristic geometrical parameters of CC2/cc-pVDZ optimized geometry of both the ground (S₀) and lowest $\pi\pi^*$ excited (S₁) states of the QFa conformers.

^a For the definition of the dihedral angles, see the Supporting Information (Figure S1). The residue 1 correspond to the first residue from the N-term.

^b The two distances correspond to the C₇ and C₁₀ H-bond distances.

^c The NH... π bond is characterized by three distances: the distance of the NH_{Phe} (A and C conformer) or NH_{2,chain} group (B conformer) hydrogen atom with the C _{γ} (A and C conformer) or C _{ξ} (B conformer) carbon atom of the phenylalanine residue and in parentheses, the two distances with the two C _{δ} carbon atoms (C _{$\delta^{\text{to C-term}}$} , C _{$\delta^{\text{to N-term}}$}) of the phenylalanine residue (A and C conformers) or with the C _{$\delta^{\text{to C-term}}$} and C _{$\epsilon^{\text{to C-term}}$} carbon atoms (B conformer).

Appendix S8: Comparison of the CC2/cc-pVDZ optimized geometry of the S_0 and S_1 states of the Fm, GFa, FFa and QFa conformers.

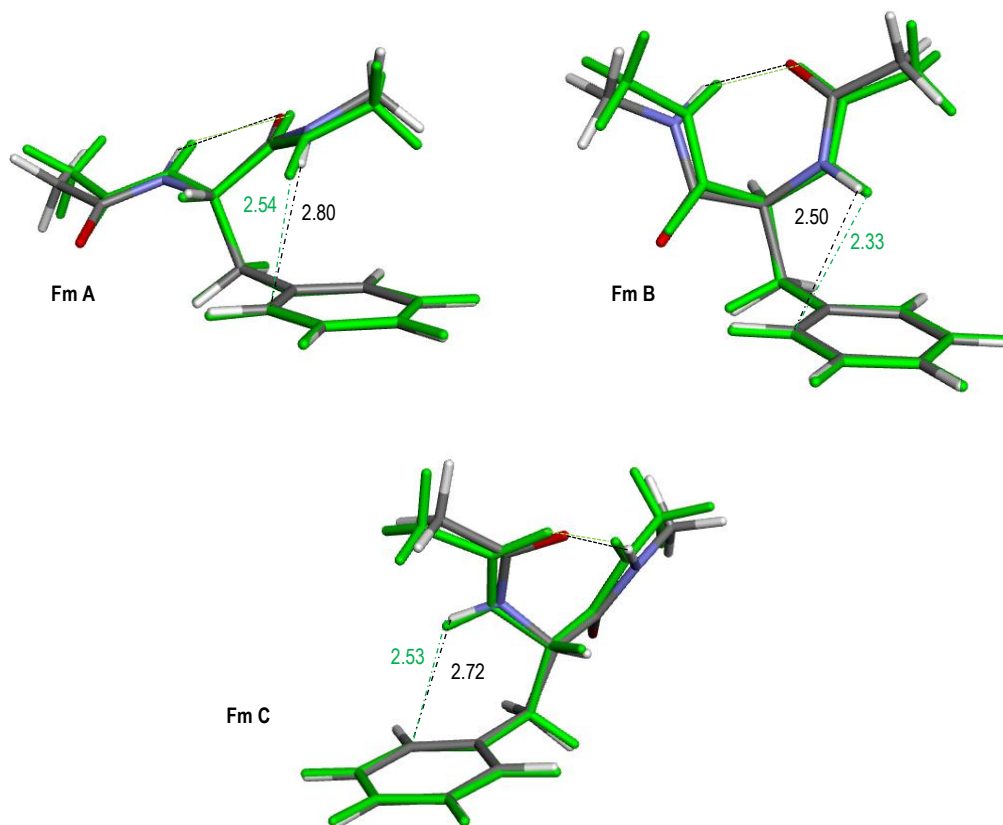


Figure S8-1: Comparison of the CC2/cc-pVDZ optimized geometry of the S_0 (atom-based colors) and S_1 states (green) of the Fm conformers. For each conformer, the phenyl rings have been overlapped. Only distances (dash-dot) that vary significantly ($|d| > 0.01 \text{ \AA}$) between the ground and the excited state (see Table S7.1) are mentioned.

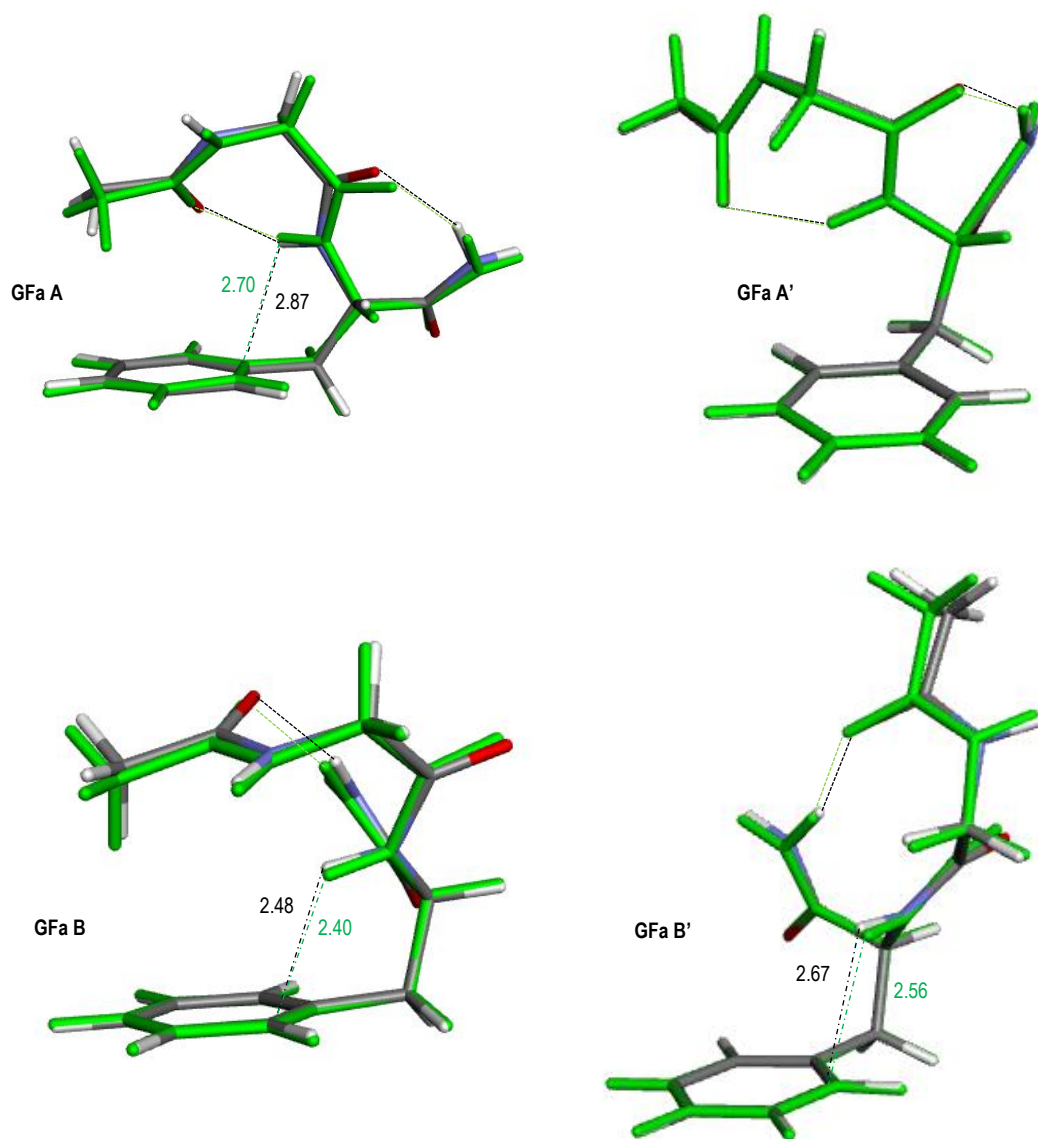


Figure S8-2: Comparison of the CC2/cc-pVDZ optimized geometry of the S₀ (atom-based colors) and S₁ states (green) of GFa A, A', B and B'. For each conformer, the phenyl rings have been overlapped. Only distances (dash-dot) that vary significantly ($|d| > 0.01$ Å) between the ground and the excited state (see Table S7.2) are mentioned.

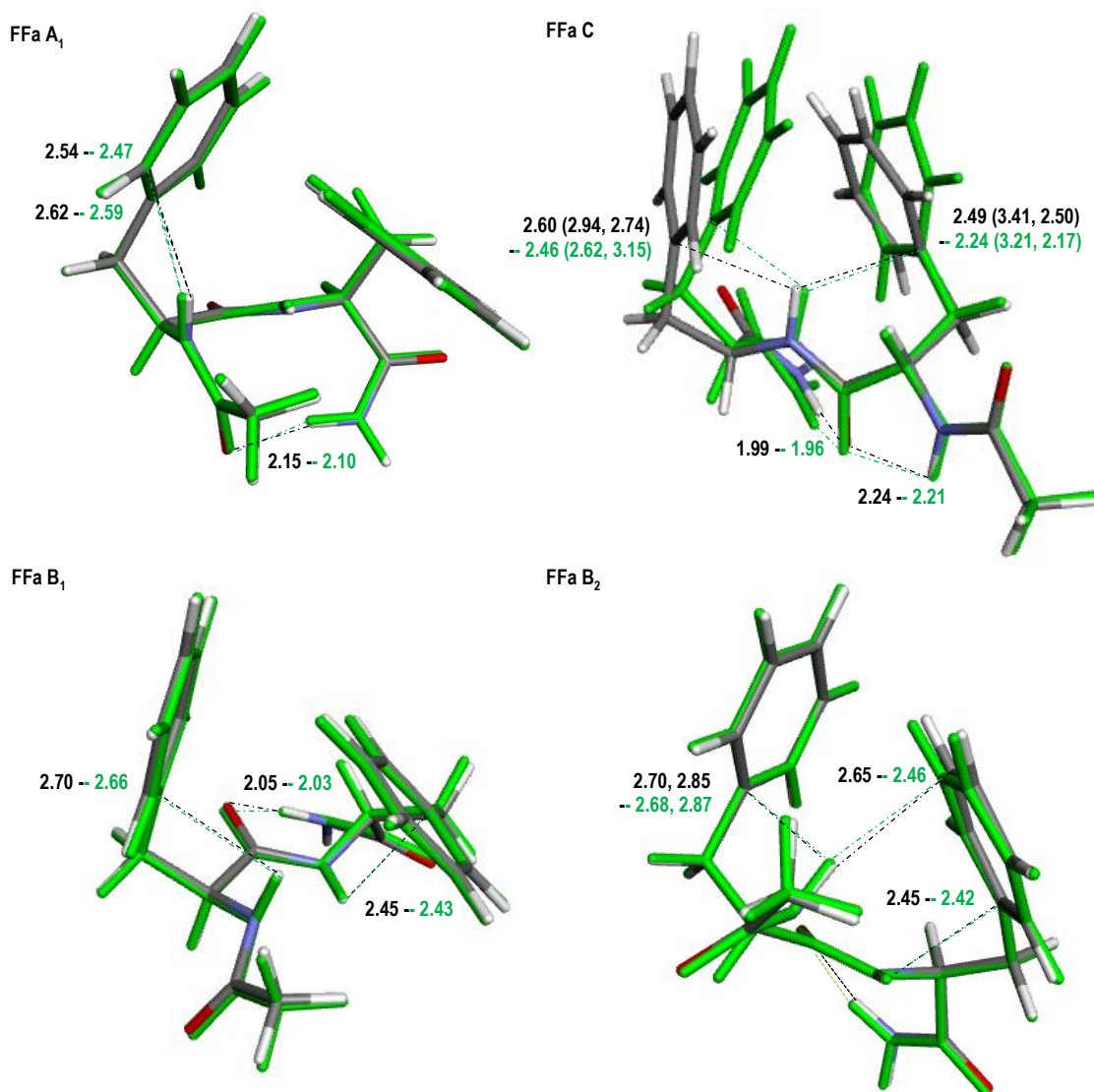


Figure S8-3: Comparison of the CC2/cc-pVDZ optimized geometry of the S₀ (atom-based colors) and S₁ states (green) of FFa A₁, B₁, B₂ and C. The phenyl rings have been overlapped for all conformers except FFa C for which this is not possible. In this latter case, the backbones until Phe1 are overlapped. Only distances (dash-dot) that vary significantly ($|d| > 0.01$ Å) between the ground and the excited state (see Table S7.3) are mentioned. In the case of FFa B₂, the distances of the NH_{Phe1} hydrogen atom with the C_ε^{to} C-term carbon atoms of Phe2 are added.

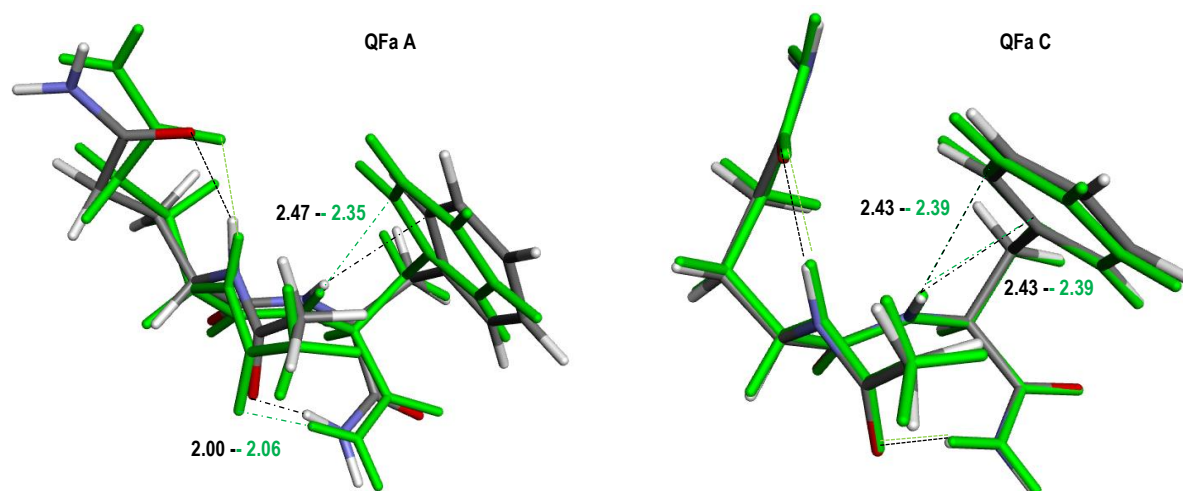


Figure S8-4: Comparison of the CC2/cc-pVDZ optimized geometry of the S_0 (atom-based colors) and S_1 states (green) of QFa A and C. For each conformer, the backbones have been overlapped. Only distances (dash-dot) that vary significantly ($|d| > 0.01$ Å) between the ground and the excited state (see Table S7.4) are mentioned.

Appendix S9: *Amide A* region frequencies of both the ground (S_0) and $\pi\pi^*$ excited (S_1) states of the Fm, GFa, FFa and QFa conformers.

Conformer/State		NH _{Phe}	NH _{C-term}
Fm A	S_1	3592	3565
	S_0	3597	3609
Fm B	S_1	3540	3463
	S_0	3587	3467
Fm C	S_1	3552	3483
	S_0	3599	3487
Experiment			
Fm A	S_1	3433	3433
	S_0	3433	3460
Fm B	S_1	3401	3342
	S_0	3433	3346

Table S9-1: CC2/cc-pVDZ *amide A* region frequencies (cm^{-1}) of both the ground (S_0) and $\pi\pi^*$ excited (S_1) states of the Fm conformers, together with the available IR experimental ones (cm^{-1}).

Conformer/State		NH _{Gln}	NH _{Phe}	NH ₂ sym./C-term	NH ₂ anti./C-term	NH ₂ sym./Chain	NH ₂ anti./Chain
QFa A	S_1	3397	3570	3529	3705	3601	3759
	S_0	3399	3582	3521	3700	3603	3761
QFa B	S_1	3415	3599	3514	3689	3522	3695
	S_0	3458	3593	3517	3688	3567	3722
QFa C	S_1	3441	3560	3517	3699	3588	3740
	S_0	3450	3576	3519	3699	3587	3739
Experiment							
QFa A	S_0	3285	3409	3365	3519	3442	3562
QFa B	S_0	3322	3445	3366	3512	3406	3527
QFa C	S_0	3336	3440	3367	3514	3426	3557

Table S9-2: CC2/cc-pVDZ *amide A* region frequencies (cm^{-1}) of both the ground (S_0) and $\pi\pi^*$ excited (S_1) states of the QFa conformers, together with the available IR experimental ones (cm^{-1}).

Conformer/State		NH _{Gly}	NH _{Phe}	NH _{2sym.}	NH _{2anti.}
GFa A	S ₁	3635	3434	3475	3675
	S ₀	3642	3452	3480	3675
GFa A'	S ₁	3645	3443	3472	3668
	S ₀	3647	3448	3474	3670
GFa B	S ₁	3643	3559	3538	3709
	S ₀	3644	3596	3541	3710
GFa B'	S ₁	3626	3582	3530	3694
	S ₀	3626	3603	3529	3695
GFa C	S ₁	3572	3569	3546	3695
	S ₀	3567	3571	3561	3709
Experiment					
GFa A	S ₁	3492	3302	3358	3510
	S ₀	3494	3320	3355	3519
GFa A'	S ₀	3495	3322	3353	3517
GFa B	S ₀	3494	3445	3391	3521
GFa B'	S ₁	3494	3423	3387	3519
	S ₀	3493	3441	3385	3518
GFa C	S ₁	3445	3408	3416	3535
	S ₀	3444	3405	3425	3541

Table S9-3: CC2/cc-pVDZ *amide A* region frequencies (cm⁻¹) of both the ground (S₀) and $\pi\pi^*$ excited (S₁) states of the GFa conformers, together with the IR available experimental ones (cm⁻¹).

Conformer/State		NH _{Phe1}	NH _{Phe2}	NH _{2sym.}	NH _{2anti.}
FFa A ₁	S ₁	3540	3587	3545	3711
FFa A ₂	S ₁	3576	3562	3547	3713
FFa A	S ₀	3581	3596	3549	3714
FFa B ₁	S ₁	3509	3552	3483	3681
FFa B ₂	S ₁	3487	3537	3489	3683
FFa B	S ₀	3520	3556	3489	3683
FFa C	S ₁	3595	3467	3458	3681
	S ₀	3607	3541	3488	3692
Experiment					
FFa A ₁	S ₁	3414	3438	3390	3524
FFa A ₂	S ₁	3446	3414	3390	3524
FFa A	S ₀	3447	3438	3391	3524
FFa B	S ₀	3412	3430	3357	3514
FFa C	S ₀	3445	3418	3382	3518

Table S9-4: CC2/cc-pVDZ *amide* A region frequencies (cm⁻¹) of both the ground (S₀) and $\pi\pi^*$ excited (S₁) states of the FFa conformers, together with the IR available experimental ones (cm⁻¹).

Appendix S10: Experimental vs. CC2/cc-pVDZ calculated harmonic *amide A* region frequencies of both the S_0 and S_1 states of the series of capped peptides and the corresponding mode-dependent linear ($v_{\text{exp.}} = av_{\text{theo.}} + b$) scaling functions.

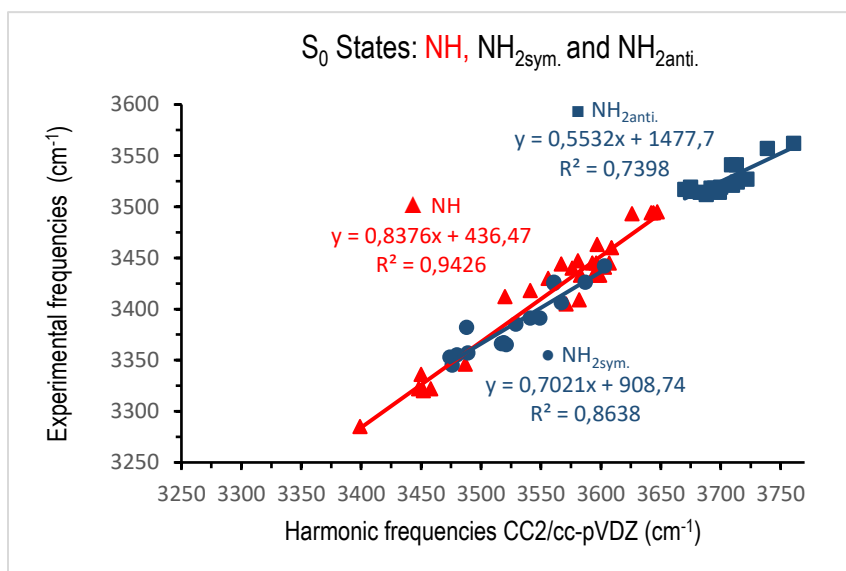


Figure S10-1: Experimental vs. CC2/cc-pVDZ calculated harmonic *amide A* region frequencies of the S_0 states of the series of capped peptides and the corresponding mode-dependent linear ($v_{\text{exp.}} = av_{\text{theo.}} + b$) scaling functions.

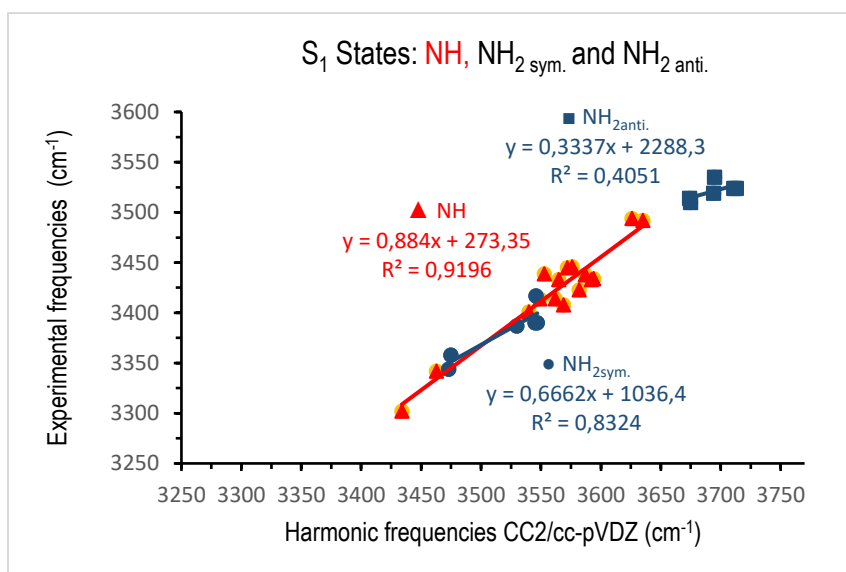


Figure S10-2: Experimental vs. CC2/cc-pVDZ calculated harmonic *amide A* region frequencies of the S_1 states of the series of capped peptides and the corresponding mode-dependent linear ($v_{\text{exp.}} = av_{\text{theo.}} + b$) scaling functions.

S11: DFT-D structures of the ground state of QFa A, B and C

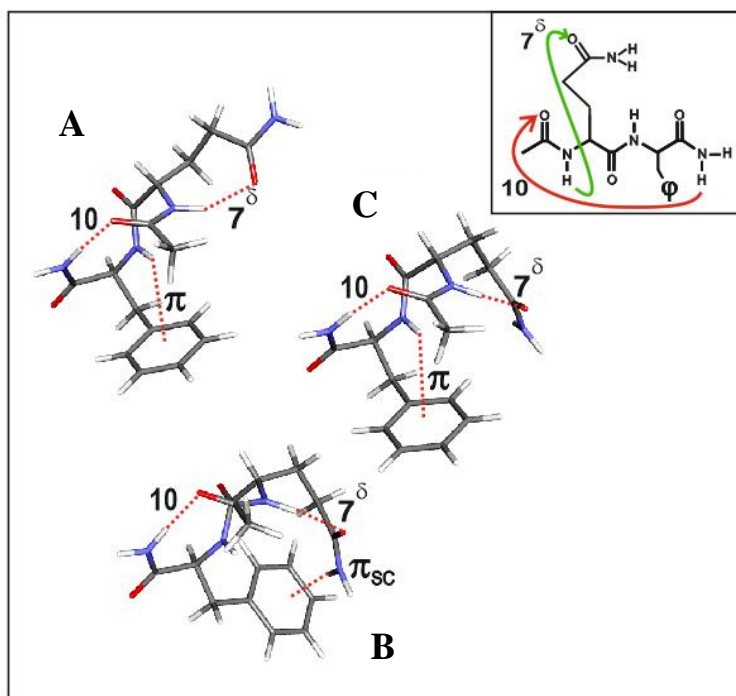


Figure S11: B97-D3 structures of the three most stable forms of QFa, which account for the conformer-selective IR spectra recorded (shown in Fig. 4). In these three forms the peptide backbone exhibits a β -turn structure stabilized by C_{10} H-bond and by a main chain/side chain H-bond, labelled 7^δ (see molecule sketch in the insert). The 3 conformers differ by the arrangement of the glutamine side chain relative to the backbone.

References:

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