Electronic Supplementary Material (ESI) for Soft Matter.

Assembly modes of hexaphenylalanine variants as function of the charge states of their terminal ends

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Peptide synthesis

F6-homosequences were synthesized according to standard solid-phase 9-fluorenylmethoxycarbonyl (Fmoc) procedures. The Rink amide MBHA resin (substitution 0.65 mmol/g) and the Wang resin preloaded with Phe (substitution 0.60 mmol/g) were used as solid phase support. Synthesis scale for all the hexaphenylalanine sequences was 0.25 mmol. The synthesis was carried out using a mixture of N,N-dimethylformamide/N-methyl-2-pyrrolidone (DMF/NMP, 1:1, v/v) as solvent phase. Before starting the peptide elongation, resins were swelled for 30 min in solvent medium. Fmoc deprotection was performed twice (each treatment for 10 min) using 30% (v/v) piperidine in DMF/NMP. The Fmoc-amino acid couplings were achieved by adding 2-fold molar excess of Fmoc-aa-OH, mixed with equimolar amounts of 1-hydroxybenzotriazole (HOBt), benzotriazol-1-yl-oxy-tris-pyrrolidino-phosphonium (PyBop) and 4-fold molar excess of diisopropylethylamine (DIPEA). All couplings were performed twice for 40 minutes. N-terminus acetylation was performed twice (each treatment for 10 minutes) using a solution of pyridine/acetic anhydride (4/4.7 v/v) in DMF. Crude homopeptides were fully cleaved in acidic condition by TFA (trifluoroacetic acid)/H_2O (95/5 v/v) mixture at room temperature for 2 hours. F6-peptides were precipitated with ice-cold water.

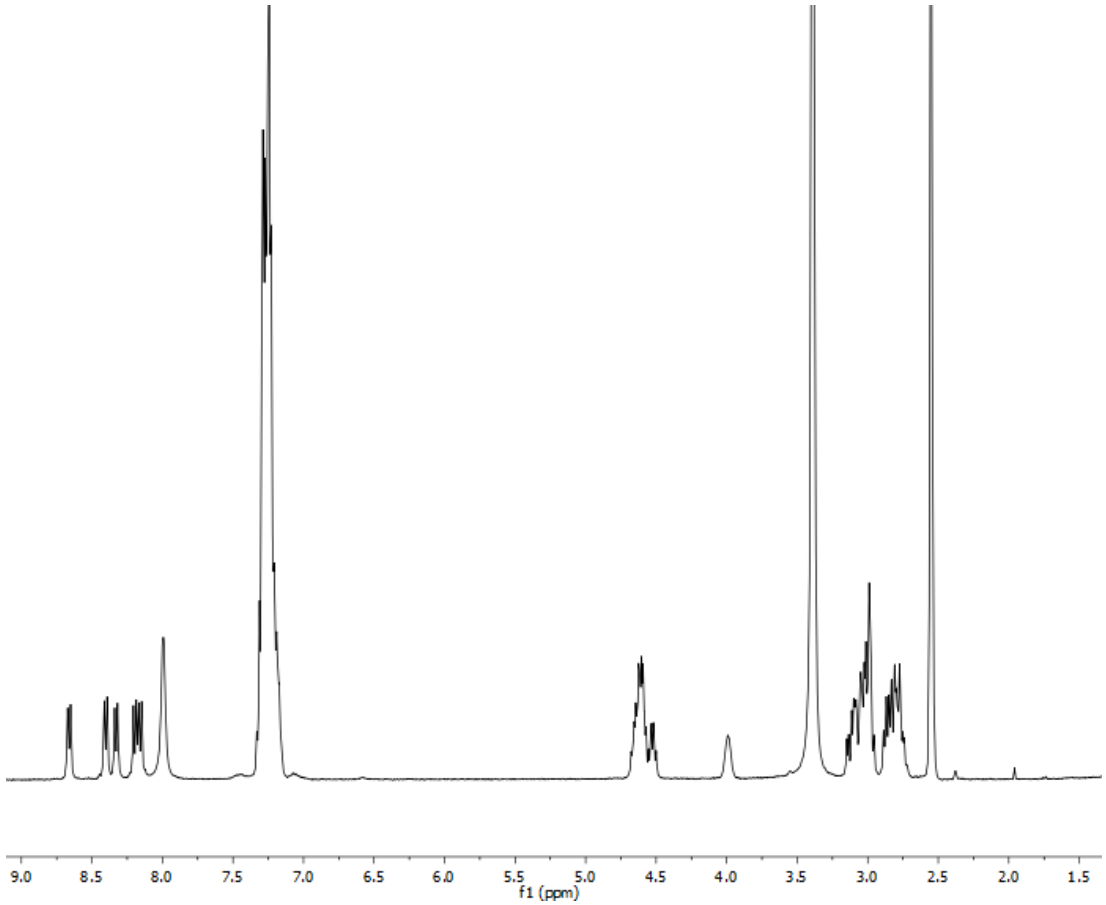


Figure S1. ^{1}HNMR spectrum for H^{+}-F6-O^{-} in DMSO-*d*6

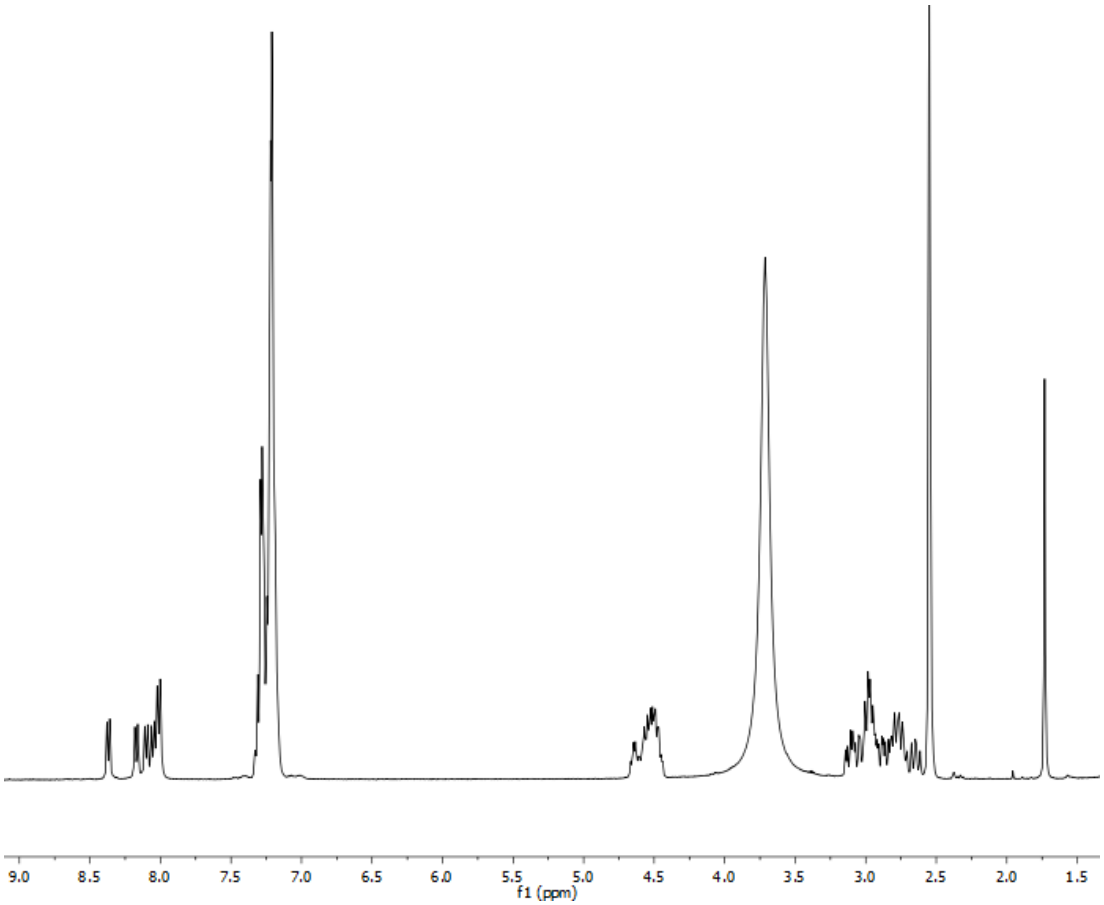


Figure S2. ^{1}HNMR spectrum for Ac-F6-O^{-} in DMSO-*d*6

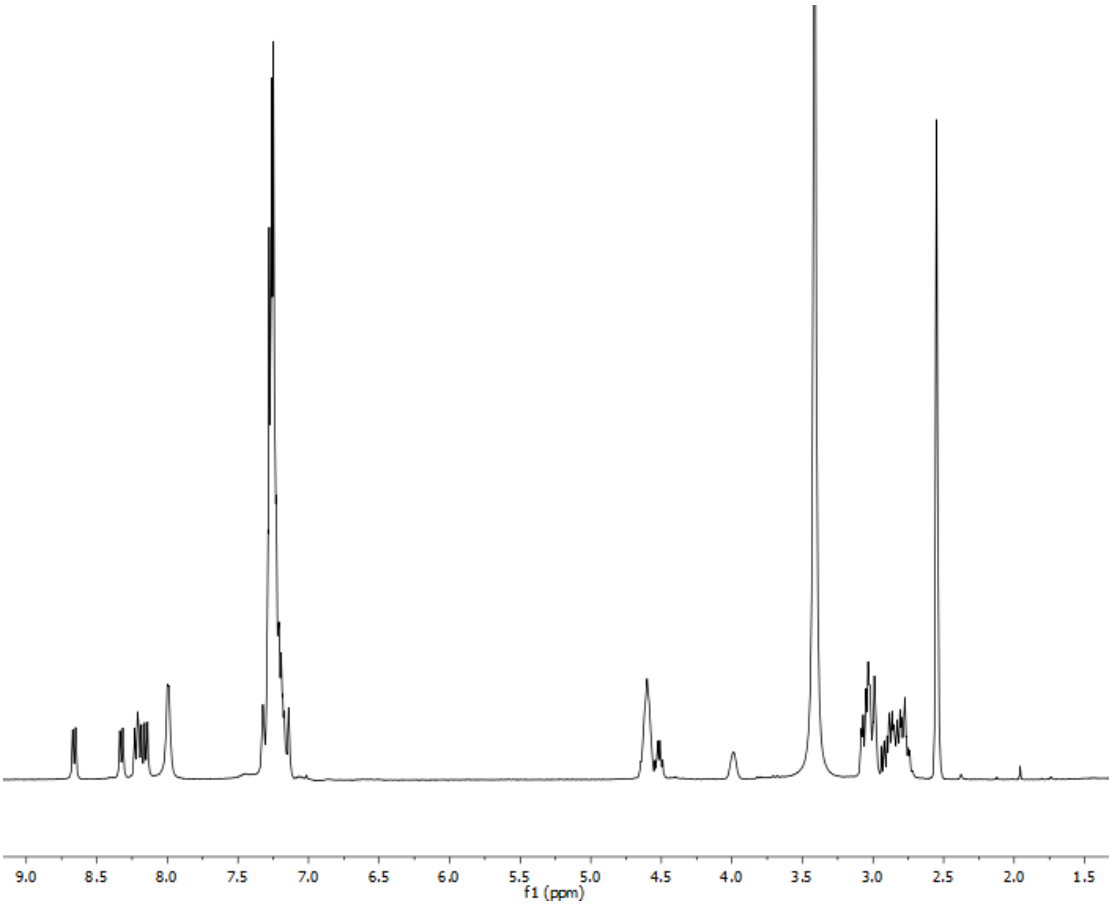


Figure S3. ^{1}HNMR spectrum for H^{+}-F6-Amide in DMSO-*d*6

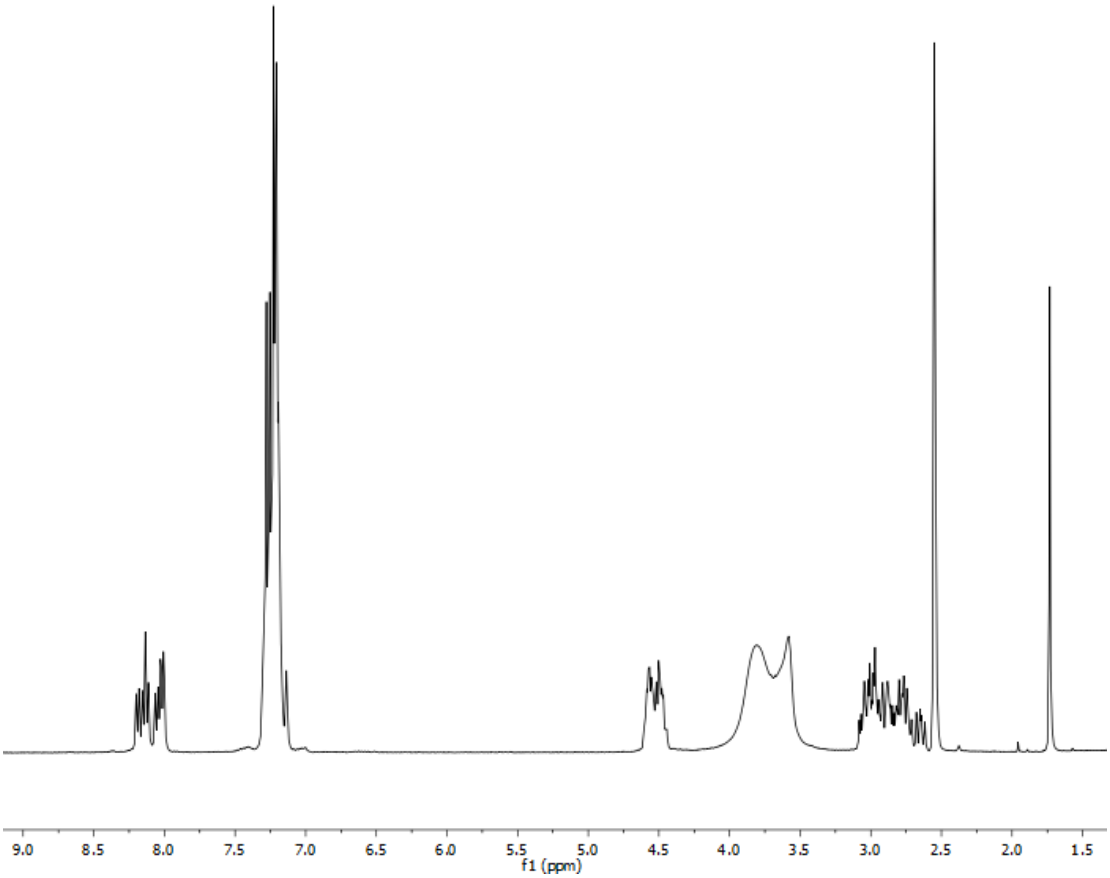


Figure S4. [1]HNMR spectrum for Ac-F6-Amide in DMSO-*d*6

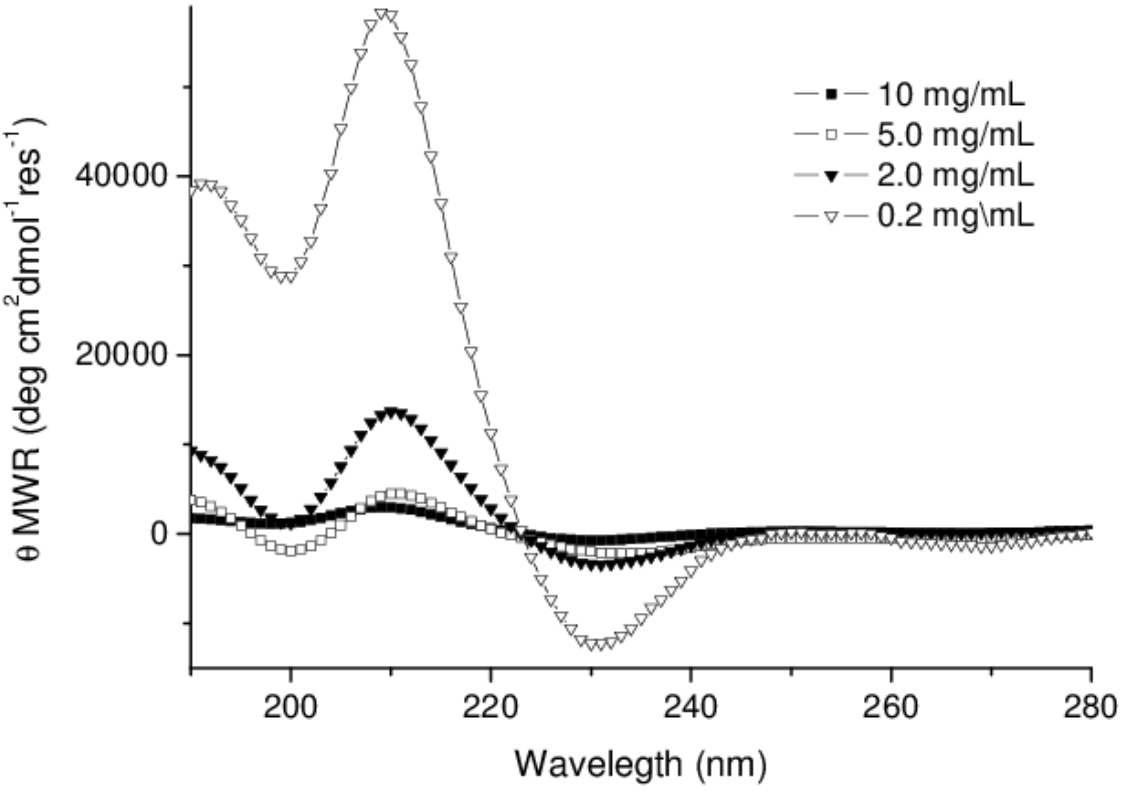


Figure S5. CD spectra of H^+-F6-O^- in MeOH at different concentrations (0.2, 2.0, 5.0 and 10 mg/mL).

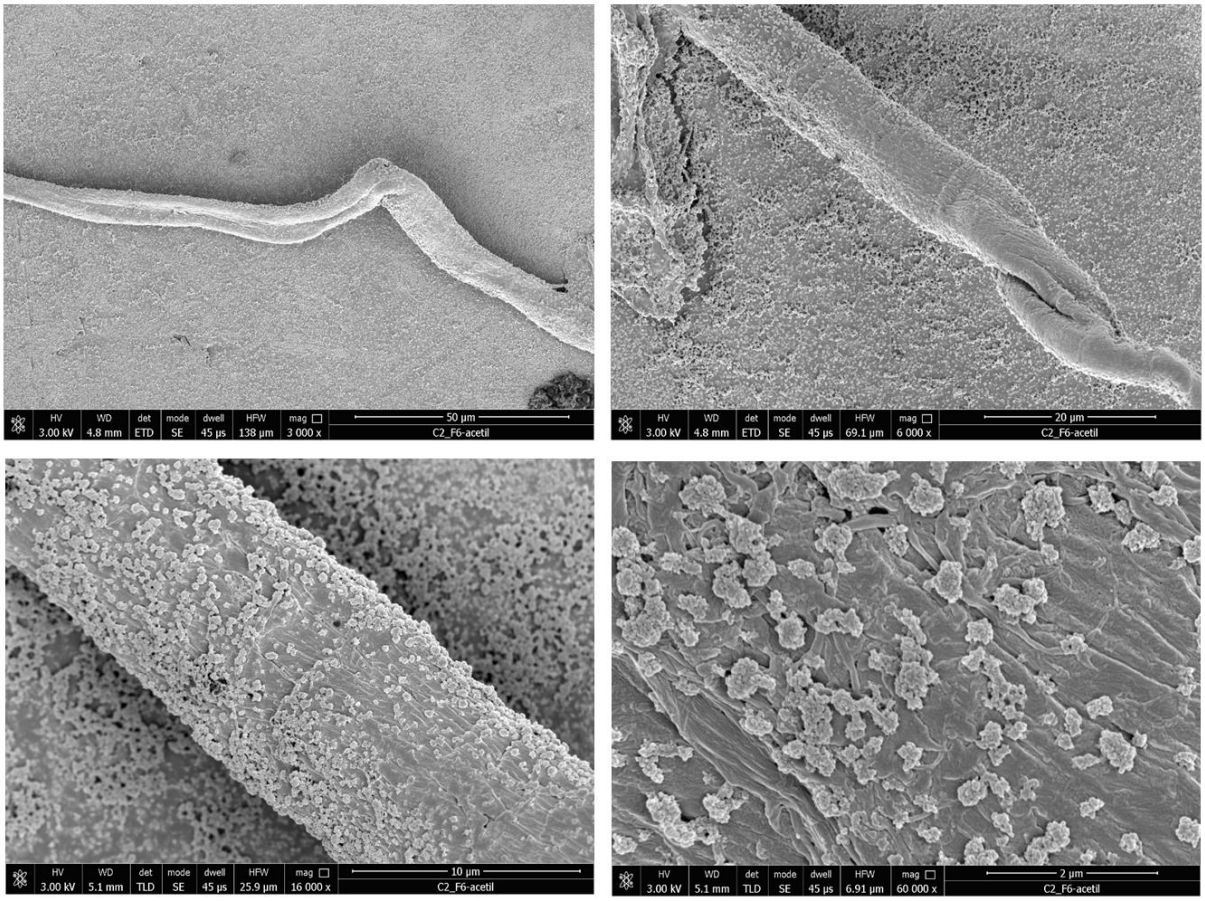


Figure S6. Micrographs of Ac-F6-Amide at 0.5 mg·mL^{-1} (3000x, 50 µm, 6000x, 20 µm, 16000x, 10 µm scale bar and 60000x, 2 µm respectively).

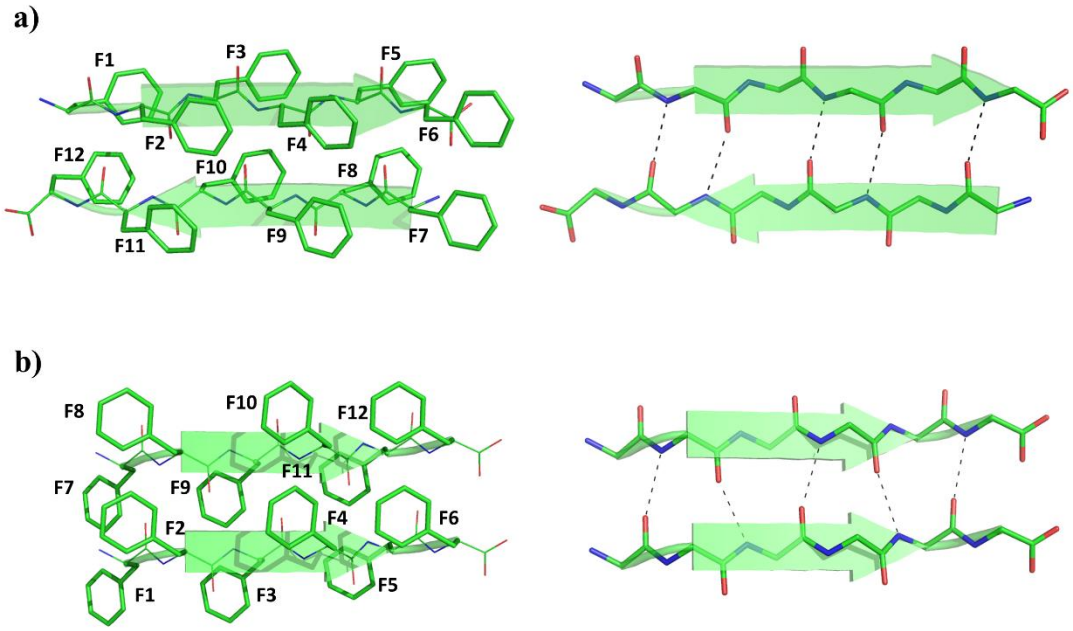
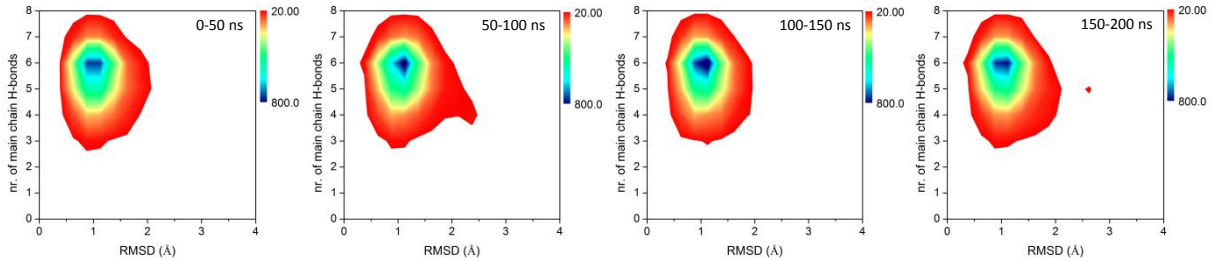


Figure S7: Parellel (a) and antiparallel (b) models of H^+-F6-O^- used as starting structures of the REMD simulation. Phe numbering (F1-F12) scheme is also reported. The H-bonding pattern of these structural motifs is reported on the right side.

a)



b)

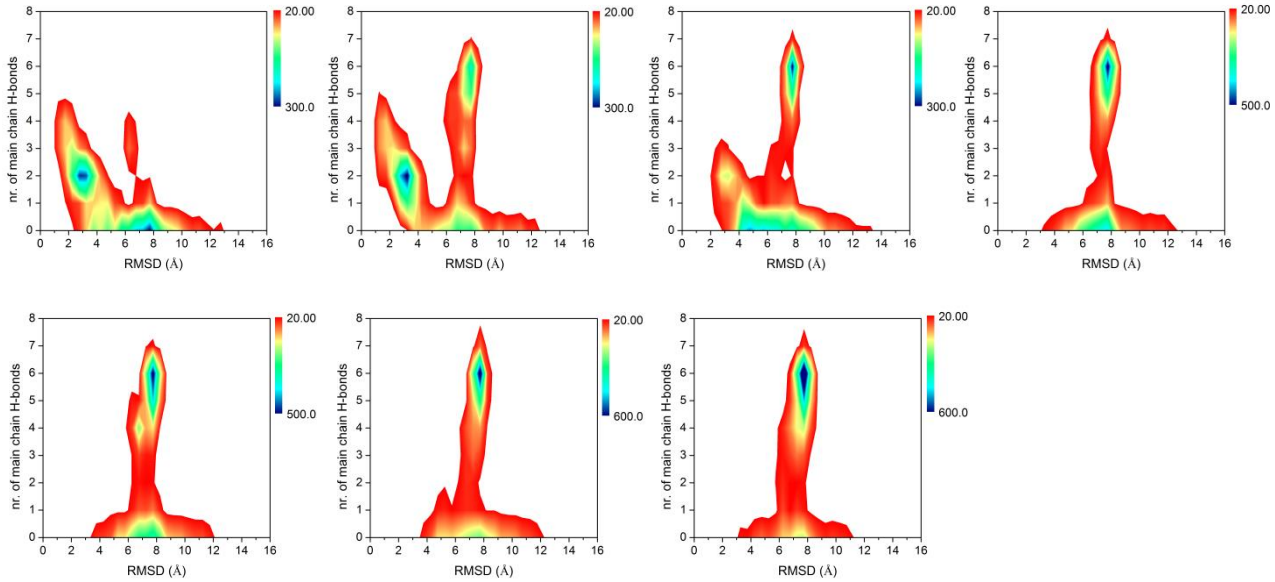


Figure S8: Ensemble of trajectory structures of the replicas at 300 K of H^+-F6-O^-_anti (a) and H^+-F6-O^-_par (b) computed in intervals of 50 ns of the whole trajectory. The RMSD values are computed against the starting models.

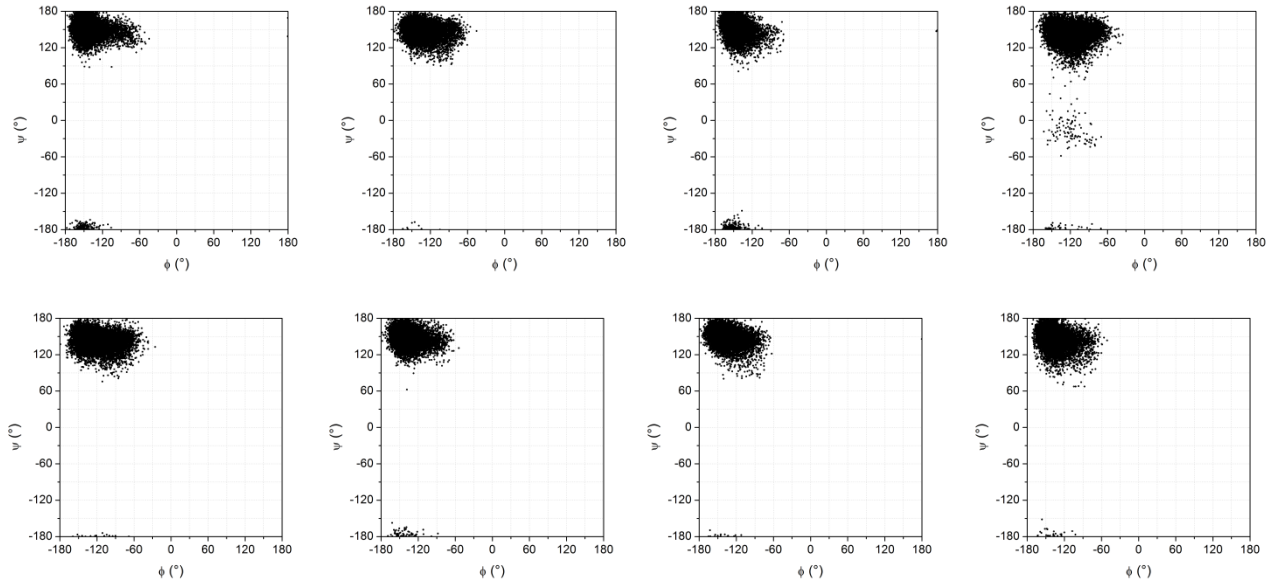


Figure S9. Ramachandran plots of non-terminal Phe residues of H^+-F6-O^-_anti REMD trajectory structures computed considering the last 100 ns of the trajectory.

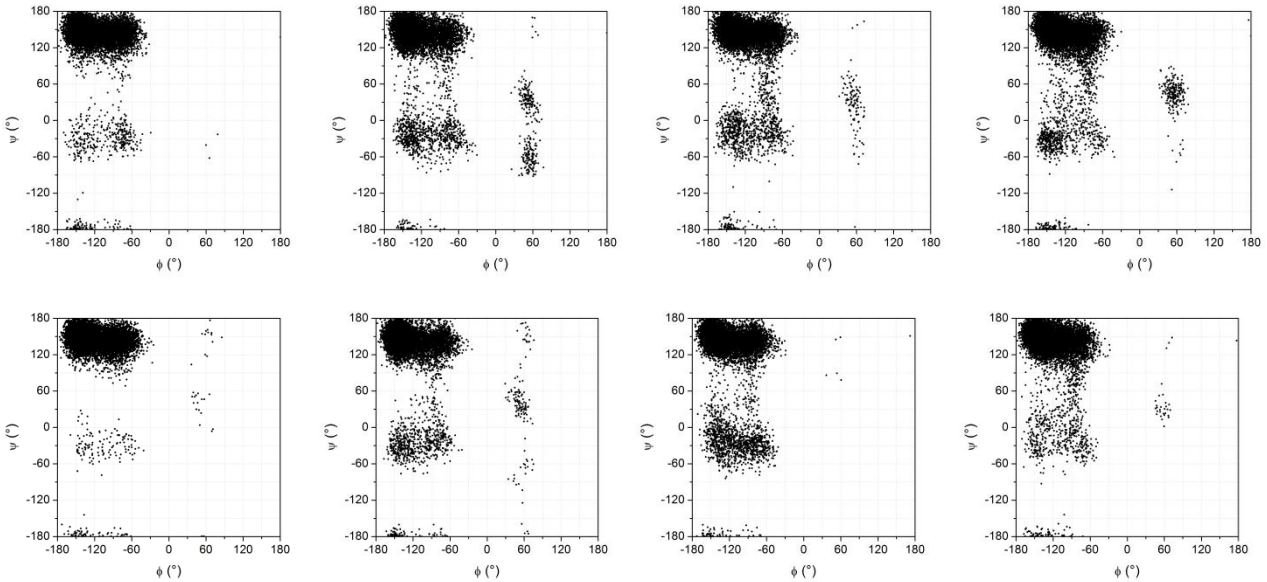
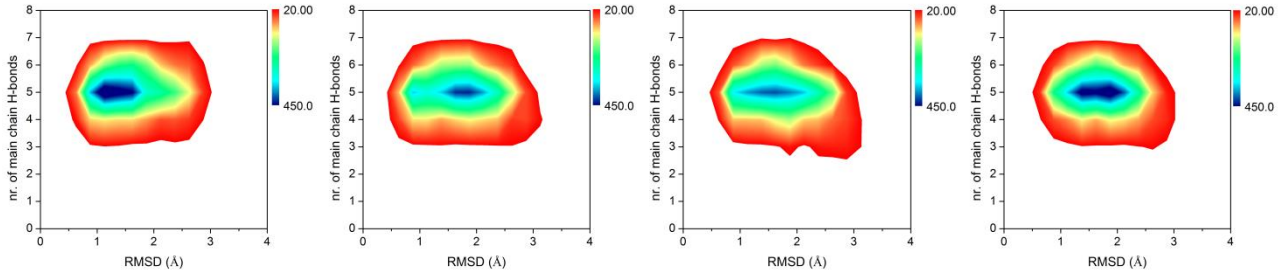


Figure S10. Ramachandran plots of non-terminal Phe residues of H^+-F6-O^-_par REMD trajectory structures computed considering the last 100 ns of the trajectory.

a)



b)

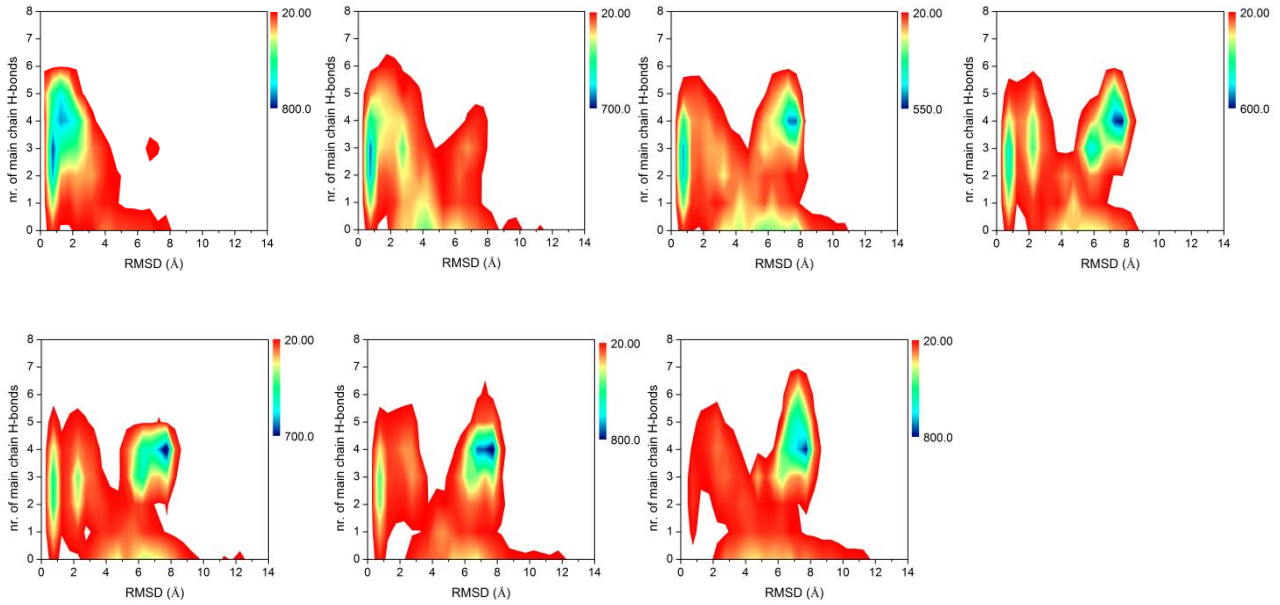


Figure S11. Ensemble of trajectory structures of the replicas at 300 K of Ac-F6-Amide_anti (a) and Ac-F6-Amide_par (b) computed in intervals of 50 ns and 100 ns of the whole trajectory, respectively. The RMSD values are computed against the starting models.

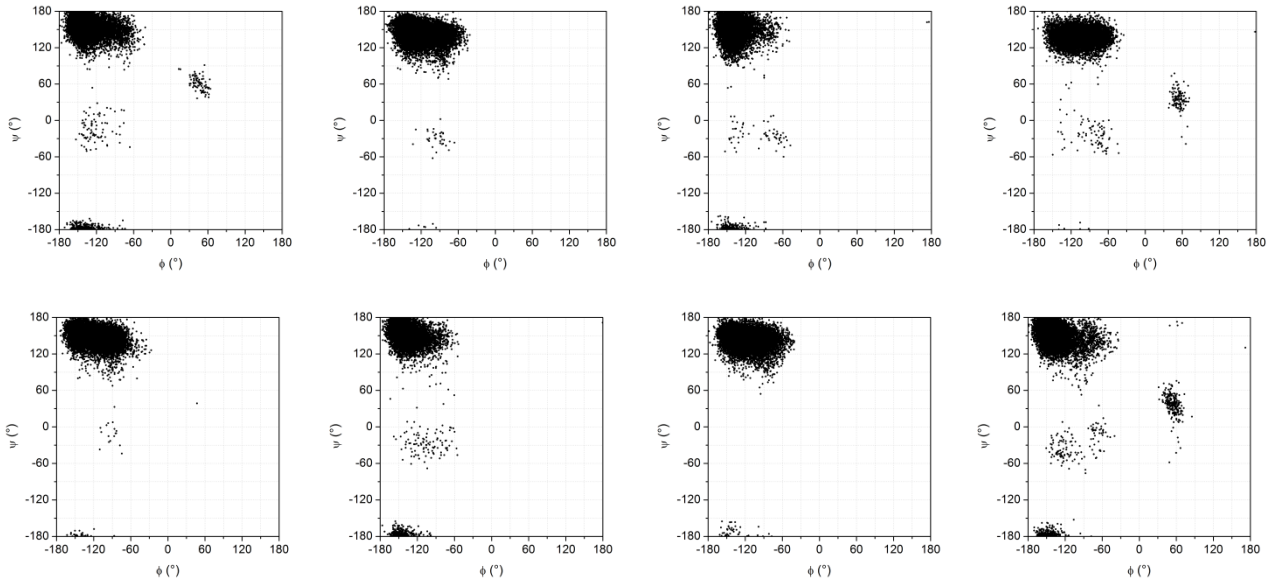


Figure S12. Ramachandran plots of non-terminal Phe residues of Ac-F6-Amide_anti REMD trajectory structures computed considering the last 100 ns of the trajectory.

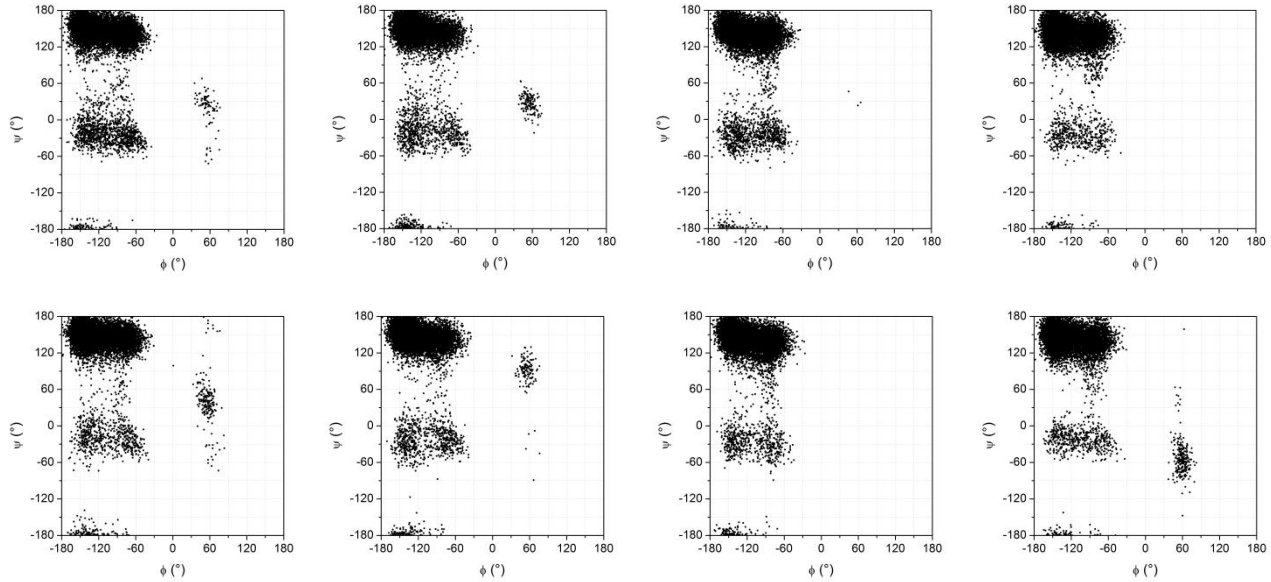


Figure S13. Ramachandran plots of non-terminal Phe residues of Ac-F6-Amide_par REMD trajectory structures computed considering the last 100 ns of the trajectory.

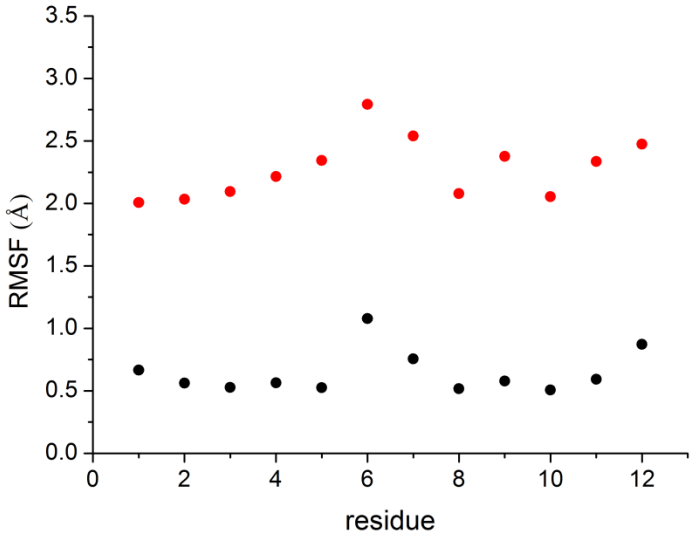


Figure S14. Root mean square fluctuation (RMSF) values of Phe residues computed considering the main chain C^{α} atoms (black) or the side chain atoms (red) in the last 100 ns interval of the H^{+}-F6-O^{-}_anti REMD simulation.

Table S1. Parameters and statistics of REMD simulations.

System (PDB)	Average exchange freq. (%)	Box dimensions (nm^3)	No. of water molecules	Simulated time per replica (ns)	RMSIP[a]
Antiparallel charged	28%	4.9x3.4x3.5	1819	200	0.97
Antiparallel uncharged	27%	5.0x3.4x3.5	1863	200	0.86
Parallel charged	27%	3.8x3.7x4.4	1895	350	0.94
Parallel uncharged	25%	3.8x3.7x4.7	2026	700	0.88

[a] The RMSI values have been calculated by dividing the last 100 ns of each trajectory in two equivalent halves.