On the stability of peptide secondary structures on the TiO₂ (101) anatase surface: a computational insight

Electronic Supplementary Information

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Table S1. Cell parameters for the linear polyamino acidic (AA) systems interacting with the TiO_2 surface, and optimized as isolated in the gas phase.

	TiO$_2$ cell parameters					AA cell parameter	
	a	b	α	β	γ	a	Diff %
GLY_linear	7.569	10.239	90.000	90.000	90.000	7.236	-4.61
ALA_linear						7.172	-5.53
GLU_linear						7.180	-5.41
ARG_linear						7.192	-5.24
LYS_linear						7.184	-5.35

Table S2. Cell parameters for the β-sheet polyamino acidic (AA) systems interacting with the TiO$_2$ surface, and optimized as isolated in the gas phase.

	TiO$_2$ cell parameters					AA cell parameters						
	a	b	α	β	γ	a	b	α	β	γ	Diff (a) %	Diff (b) %
GLY_β-sheet_AP	7.569	10.239	90.000	90.000	90.000	7.278	9.693	89.997	90.008	90.000	-4.00	-5.64
GLY_β-sheet_P						7.264	10.108	90.000	90.006	90.023	-4.20	-1.30
ALA_β-sheet_AP						7.097	9.552	90.000	90.179	90.028	-6.65	-7.19
ALA_β-sheet_P						7.149	9.948	91.111	89.936	89.894	-5.88	-2.93
GLU_β-sheet_AP						7.076	9.552	90.096	89.055	89.943	-6.97	-7.20
GLU_β-sheet_P						7.152	9.733	89.720	89.651	89.990	-5.83	-5.20
ARG_β-sheet_AP						7.055	9.559	89.996	89.666	89.131	-7.28	-7.11
ARG_β-sheet_P						7.090	9.308	86.053	87.268	89.607	-6.75	-10.01
LYS_β-sheet_AP						7.056	9.606	87.096	87.371	90.468	-7.27	-6.59
LYS_β-sheet_P						7.083	9.793	84.047	90.983	89.914	-6.87	-4.56

Table S3. Cell parameters for the α-helix polyamino acidic (AA) systems interacting with the TiO$_2$ surface, and optimized as isolated in the gas phase.

	TiO$_2$ cell parameters					AA cell parameters	
	a	b	α	β	γ	b	Diff %
GLY_α-helix	15.138	10.239	90.000	90.000	90.000	10.424	1.78
ALA_α-helix						10.429	1.82
GLU_α-helix						10.393	1.48
ARG_α-helix						10.405	1.59
LYS_α-helix						10.392	1.47

Table S4. Calculated total adsorption energies (ΔE_{ADS}) and adsorption energy normalized per amino acidic unit ($\Delta E_{ADS/unit}$) for each studied complex, both in the gas phase and under PCM conditions. Other energetic terms of interest are also included: the energetic gain due to the secondary structure formation with respect to the extended primary polymeric structure ($\Delta E_{H/unit}$), the deformation energy of the secondary structure due to the adsorption ($\Delta E_{def/unit}$), and the sum of these two terms ($\Delta E_{H+def/unit}$). Energy units are in kJ mol^{-1}.

System	AA units	Gas-phase					PCM				
		ΔE_{ADS}	$\Delta E_{ADS/unit}$	$\Delta E_{H/unit}$	$\Delta E_{def/unit}$	$\Delta E_{H+def/unit}$	ΔE_{ADS}	$\Delta E_{ADS/unit}$	$\Delta E_{H/unit}$	$\Delta E_{def/unit}$	$\Delta E_{H+def/unit}$
GLY_extended/TiO$_2$	2	-62.0	-31.0	0.0	15.3	15.3	-3.8	-1.9	0.0	13.7	13.7
GLY_β-sheet_AP/TiO$_2$	4	-120.8	-30.2	-23.6	23.0	-0.6	-0.5	-0.1	-9.1	19.7	10.6
GLY_β-sheet_P/TiO$_2$	4	-115.6	-28.9	-18.5	19.6	1.1	-3.6	-0.9	-3.8	13.8	10.0
GLY_β-sheet_BRK/TiO$_2$	4	-123.2	-30.8	0.0	11.8	11.8	-16.4	-4.1	0.0	10.4	10.4
GLY_α-helix_1/TiO$_2$	7	-220.5	-31.5	-21.5	8.6	-12.9	-84.1	-12.0	-9.9	5.9	-4.0
GLY_α-helix/TiO$_2$	7	-235.9	-33.7	-21.5	14.1	-7.4	-80.8	-11.5	-9.9	9.4	-0.5
ALA_extended/TiO$_2$	2	-63.4	-31.7	0.0	18.6	18.6	-2.9	-1.5	0.0	17.4	17.4
ALA_β-sheet_AP/TiO$_2$	4	-69.7	-17.4	-27.4	22.2	-5.2	15.3	3.8	-14.5	21.5	6.9
ALA_β-sheet_P/TiO$_2$	4	-61.9	-15.5	-20.9	17.2	-3.7	16.7	4.2	-9.8	18.5	8.7
ALA_α-helix/TiO$_2$	7	-186.1	-26.6	-23.2	5.2	-18.0	-79.3	-11.3	-11.9	5.1	-6.8

GLU_extended/TiO$_2$	2	-109.6	-54.8	0.0	25.8	25.8	7.6	3.8	0.0	22.0	22.0
GLU_β-sheet_AP/TiO$_2$	4	-228.5	-57.1	-37.6	34.9	-2.7	-75.1	-18.8	-20.9	36.1	15.2
GLU_β-sheet_P/TiO$_2$	4	-262.0	-65.5	-36.8	30.0	-6.8	-93.5	-23.4	-10.2	22.5	12.3
GLU_α-helix/TiO$_2$	7	-412.8	-59.0	-31.6	12.4	-19.3	-141.3	-20.2	-15.1	10.7	-4.4
LYS_extended/TiO$_2$	2	-217.3	-108.6	0.0	50.8	50.8	-73.9	-36.9	0.0	48.9	48.9
LYS_β-sheet_AP/TiO$_2$	4	-270.7	-67.7	-39.3	29.1	-10.2	-154.9	-34.3	-22.3	25.7	3.4
LYS_β-sheet_P/TiO$_2$	4	-286.9	-71.7	-36.4	24.2	-12.1	-137.3	-38.7	-19.7	21.4	1.6
LYS_α-helix/TiO$_2$	7	-589.5	-84.2	-23.3	9.8	-13.5	-323.3	-46.2	-10.1	11.1	1.0
ARG_extended/TiO$_2$	2	-293.6	-146.8	0.0	46.6	46.6	-136.1	-68.1	0.0	40.5	40.5
ARG_β-sheet_AP/TiO$_2$	4	-271.7	-67.9	-60.9	59.0	-1.9	-114.0	-28.5	-29.1	43.5	14.4
ARG_β-sheet_P/TiO$_2$	4	287.3	-71.8	-74.8	64.2	-10.6	-140.3	-35.1	-30.0	34.1	4.1
ARG_α-helix/TiO$_2$	7	578.4	-82.6	-23.5	3.8	-19.7	-270.2	-38.6	-8.8	8.0	-0.9

Table S5. Values of the reaction eneries (in kJ/mol) of the α-helix → β-sheet conformational change of the isolated secondary structures and on the the TiO$_2$ (101) anatase surface ($\Delta\Delta E_{surf/unit}$), including the involved energy terms according to the energy cycle shown in Figure 4, both in the gas phase and in implicit PCM water solvent ($\Delta\Delta E_{surf/unit} = \Delta E_{ADS/unit}^{(\beta)} - \Delta E_{ADS/unit}^{(\alpha)} + \Delta\Delta E_{iso/unit}$). See in the text and in ESI the details on the definition of the energy terms.

Reaction	Conditions	$\Delta E_{ADS/unit}^{(\beta)}$	$\Delta E_{ADS/unit}^{(\alpha)}$	$\Delta\Delta E_{iso/unit}$	$\Delta\Delta E_{surf/unit}$
GLY_α-helix/TiO$_2$ → GLY_β-sheet_AP/TiO$_2$	Gas-phase	-6.6	-12.2	-2.1	3.5
	PCM	9.0	-1.6	0.8	11.4
GLY_α-helix/TiO$_2$ → GLY_β-sheet_P/TiO$_2$	Gas-phase	-10.4	-12.2	3.0	4.8
	PCM	2.9	-1.6	6.1	10.6
GLY_α-helix_1/TiO$_2$ → GLY_β-sheet_AP/TiO$_2$	Gas-phase	-6.6	-9.9	-2.1	1.2
	PCM	9.0	-2.1	0.8	11.9
GLY_α-helix_1/TiO$_2$ → GLY_β-sheet_P/TiO$_2$	Gas-phase	-10.4	-9.9	3.0	2.5
	PCM	2.9	-2.1	6.1	11.1
ALA_α-helix/TiO$_2$ → ALA_β-sheet_AP/TiO$_2$	Gas-phase	10.0	-3.3	-4.2	9.2
	PCM	18.7	0.5	-2.6	15.5
ALA_α-helix/TiO$_2$ → ALA_β-sheet_P/TiO$_2$	Gas-phase	5.5	-3.3	2.3	11.1
	PCM	13.6	0.5	2.1	15.2
GLU_α-helix/TiO$_2$ → GLU_β-sheet_AP/TiO$_2$	Gas-phase	-19.6	-27.3	-5.9	1.8
	PCM	2.1	-5.1	-5.8	1.4
GLU_α-helix/TiO$_2$ → GLU_β-sheet_P/TiO$_2$	Gas-phase	-28.7	-27.3	-5.2	-6.5
	PCM	-13.2	-5.1	5.0	-3.2
LYS_α-helix/TiO$_2$ → LYS_β-sheet_AP/TiO$_2$	Gas-phase	-28.4	-60.9	-16.0	16.5
	PCM	-12.0	-36.1	-12.2	11.9
LYS_α-helix/TiO$_2$ → LYS_β-sheet_P/TiO$_2$	Gas-phase	-35.4	-60.9	-13.1	12.5
	PCM	-19.0	-36.1	-9.7	7.5
ARG_α-helix/TiO$_2$ → ARG_β-sheet_AP/TiO$_2$	Gas-phase	-7.0	-59.1	-37.4	14.7
	PCM	0.6	-29.8	-20.3	10.1
ARG_α-helix/TiO$_2$ → ARG_β-sheet_P/TiO$_2$	Gas-phase	3.0	-59.1	-51.3	10.8
	PCM	-5.1	-29.8	-21.1	3.5
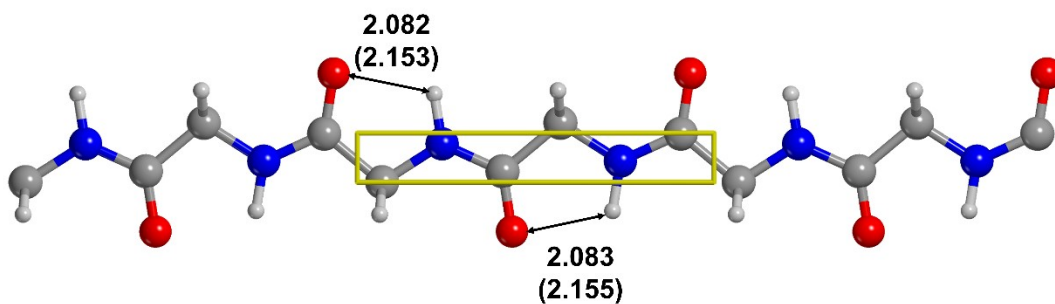
Figure S1. PBE-D2* optimized geometry for the isolated periodic linear polyglycine polymer (GLY_linear). Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM. The unit cell is represented in yellow. Bond distances are in Å. Hydrogen in white, carbon in grey, oxygen in red, nitrogen in blue.
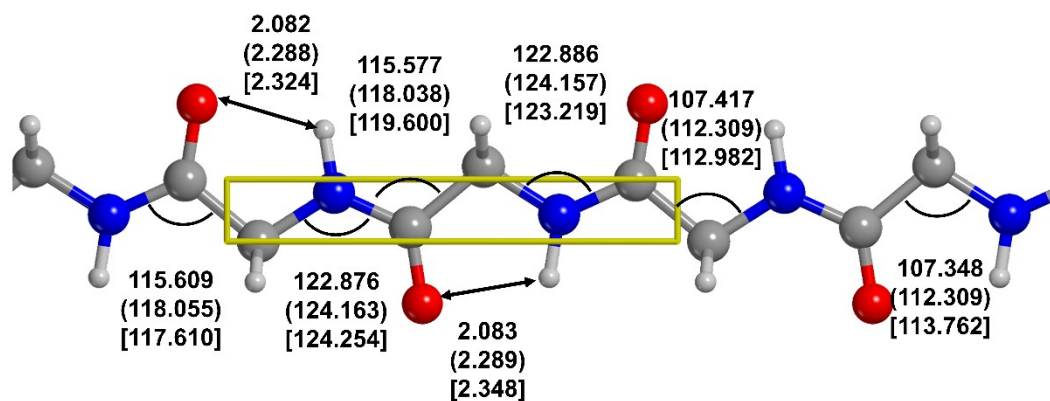
Figure S2. PBE-D2* optimized geometries of the fully optimized isolated periodic linear polyglycine polymer (GLY_linear, geometrical parameters without parenthesis), of the isolated periodic linear polyglycine polymer, using the cell parameters of the surface (geometrical parameters in round paranthesis), and upon adsorption on the TiO_2 surface (geometrical parameters in square parenthesis). The unit cell is represented in yellow. Bond distances are in Å. Hydrogen in white, carbon in grey, oxygen in red, nitrogen in blue.
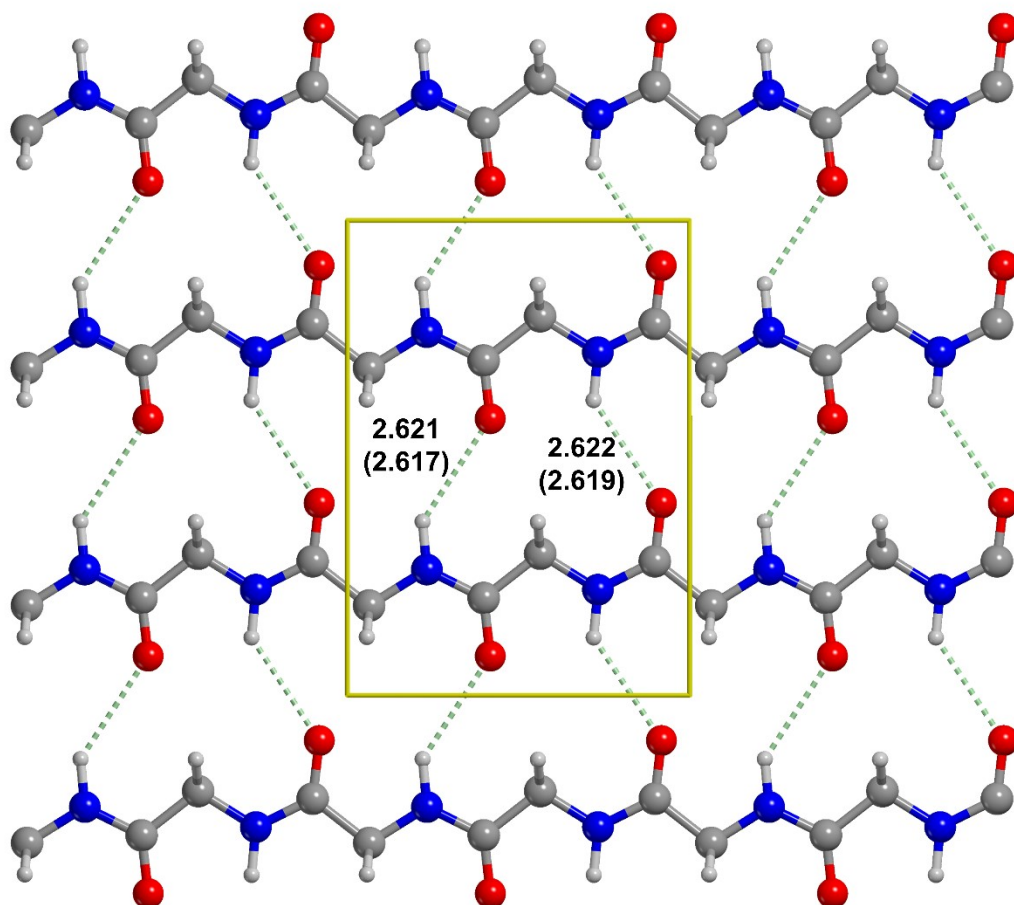
Figure S3. PBE-D2* optimized geometry for the isolated periodic parallel polyglycine β-sheet (GLY_β-sheet_P). Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM. The unit cell is represented in yellow. Bond distances are in Å. Hydrogen in white, carbon in grey, oxygen in red, nitrogen in blue.
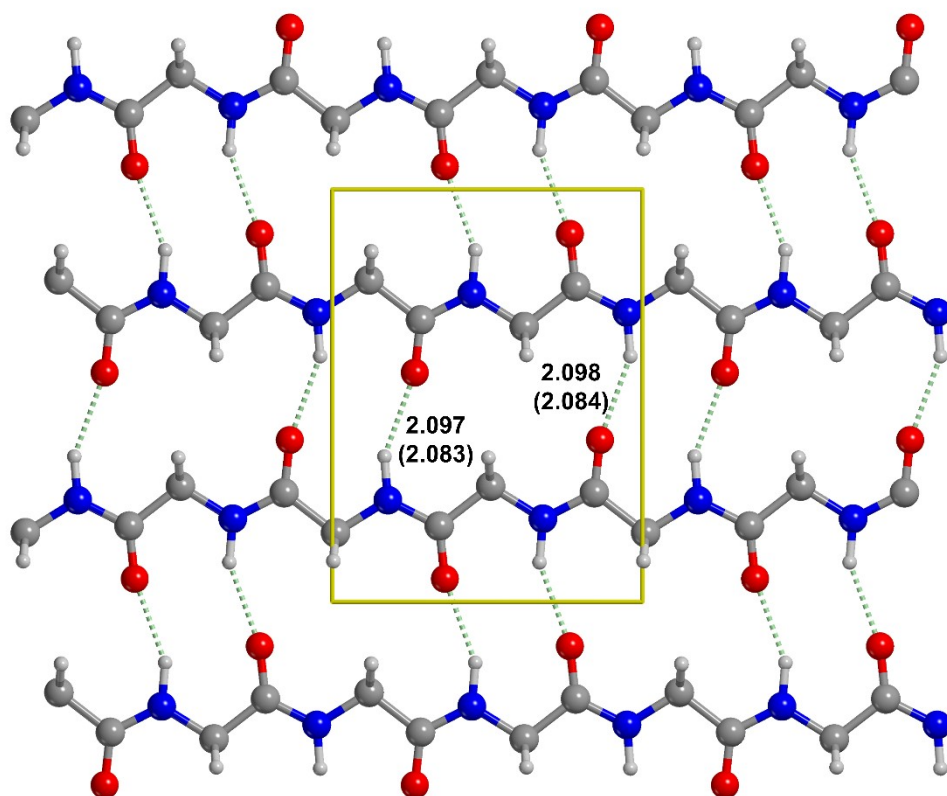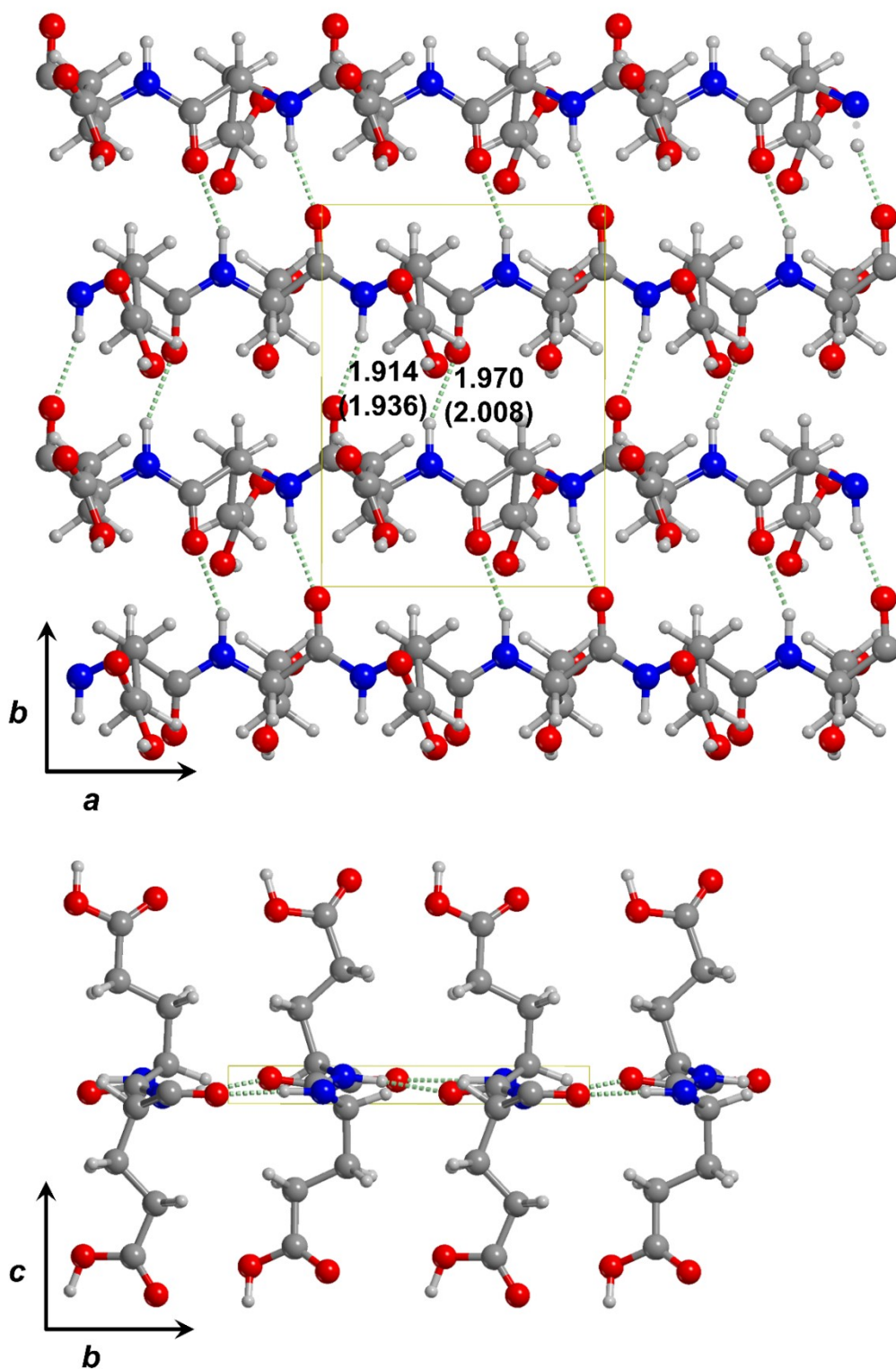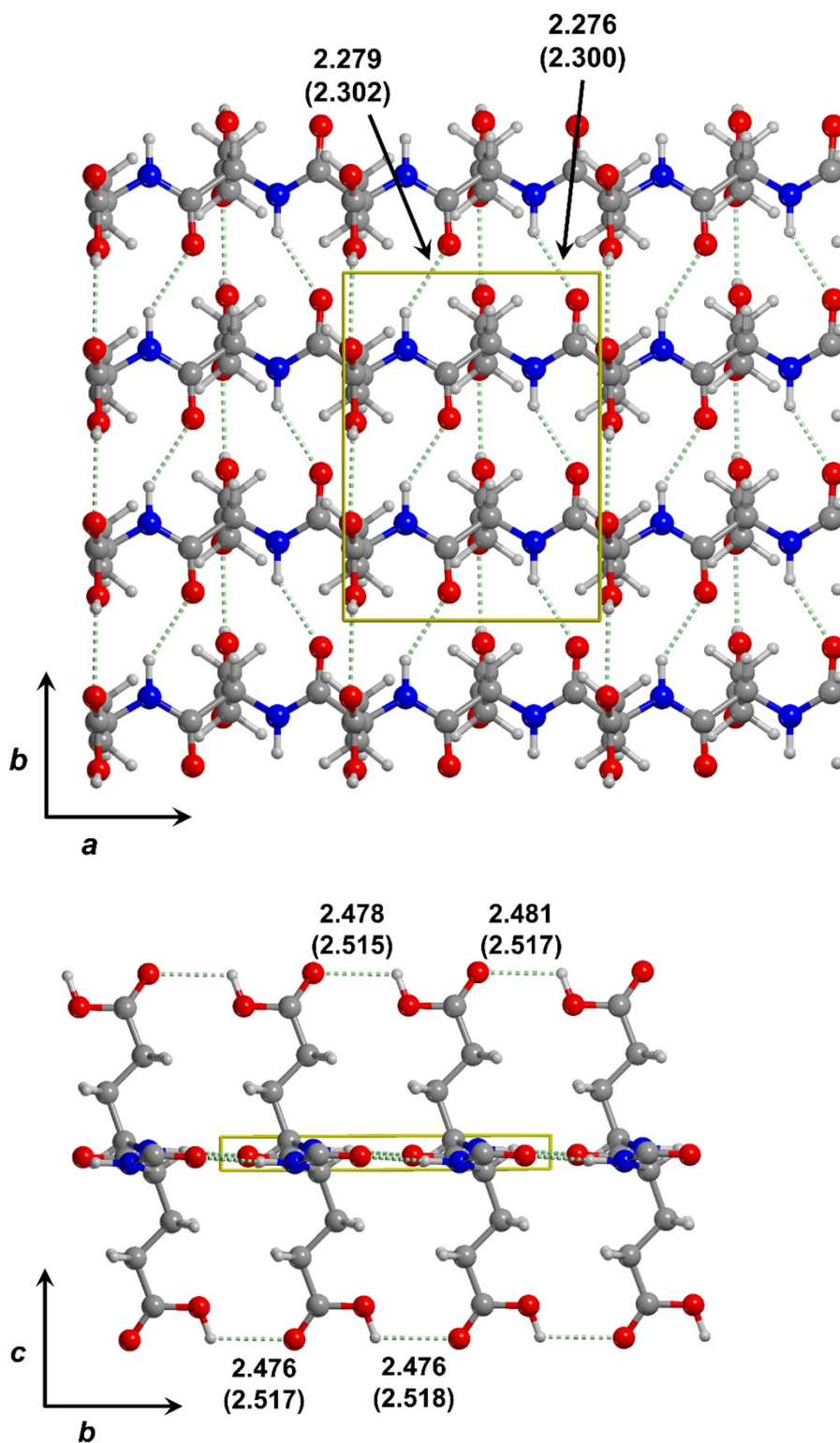
Figure S4. PBE-D2* optimized geometry for the isolated periodic antiparallel polyglycine β-sheet (GLY_β-sheet_AP). Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM. The unit cell is represented in yellow. Bond distances are in Å. Hydrogen in white, carbon in grey, oxygen in red, nitrogen in blue.
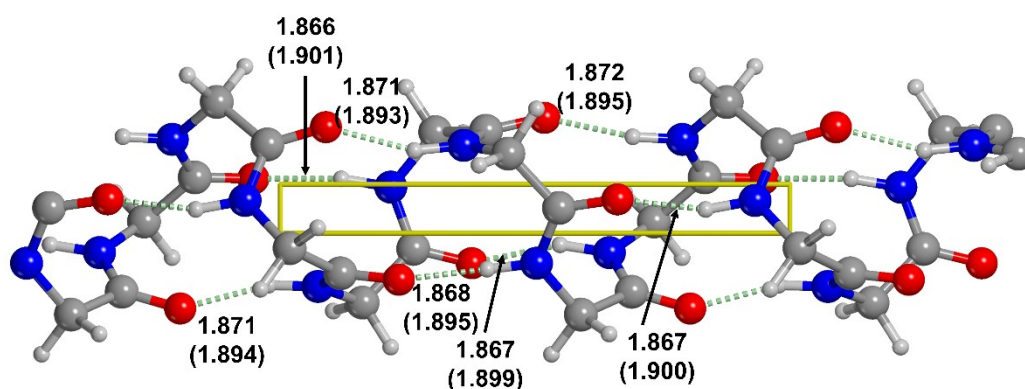
Figure S5. PBE-D2* optimized geometry for the isolated periodic polyglycine α-helix (GLY_α-helix). Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM. The unit cell is represented in yellow. Bond distances are in Å. Hydrogen in white, carbon in grey, oxygen in red, nitrogen in blue.
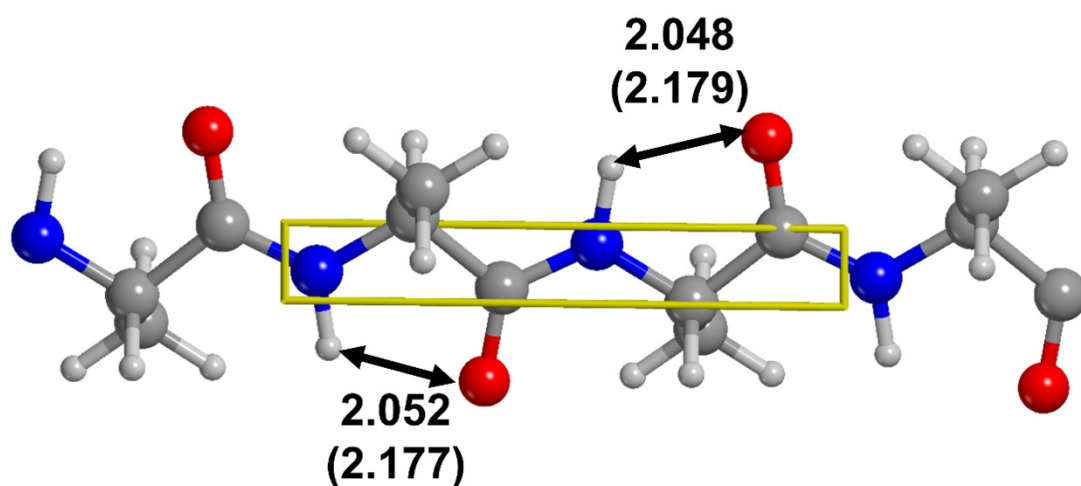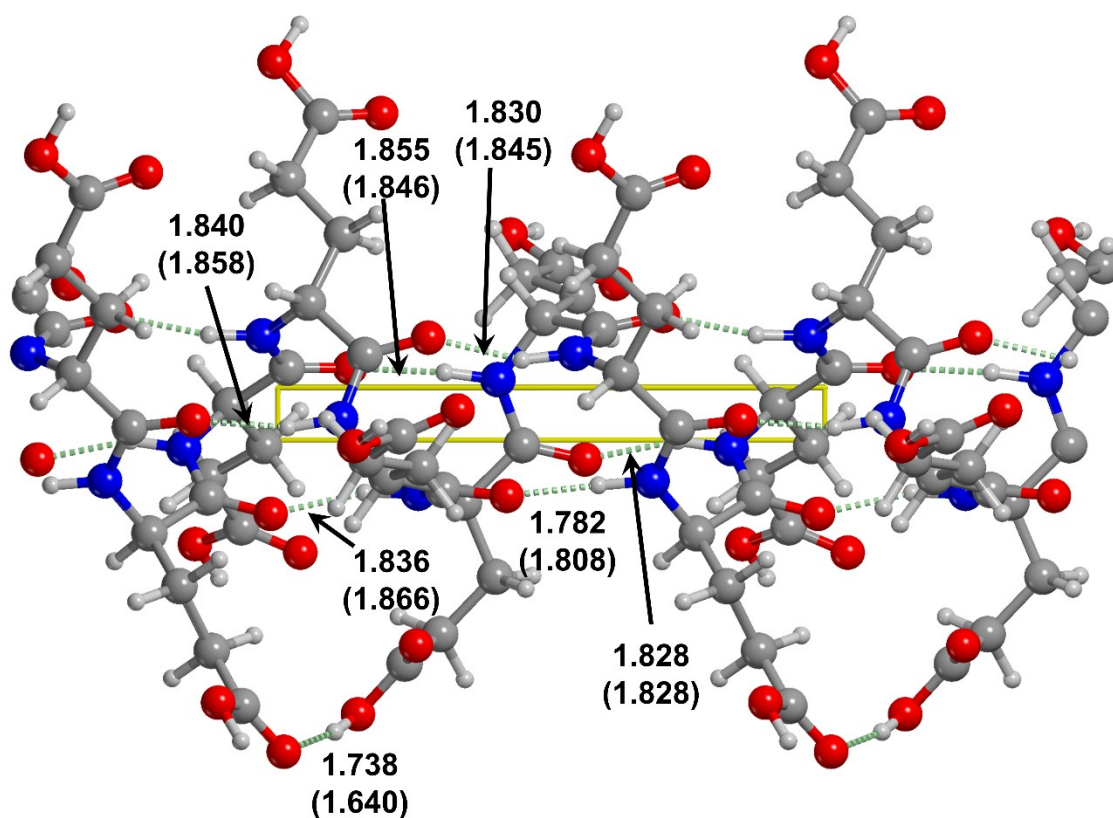
Figure S6. PBE-D2* optimized geometry for the isolated periodic linear polyalanine polymer (ALA_linear). Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM. The unit cell is represented in yellow. Bond distances are in Å. Hydrogen in white, carbon in grey, oxygen in red, nitrogen in blue.
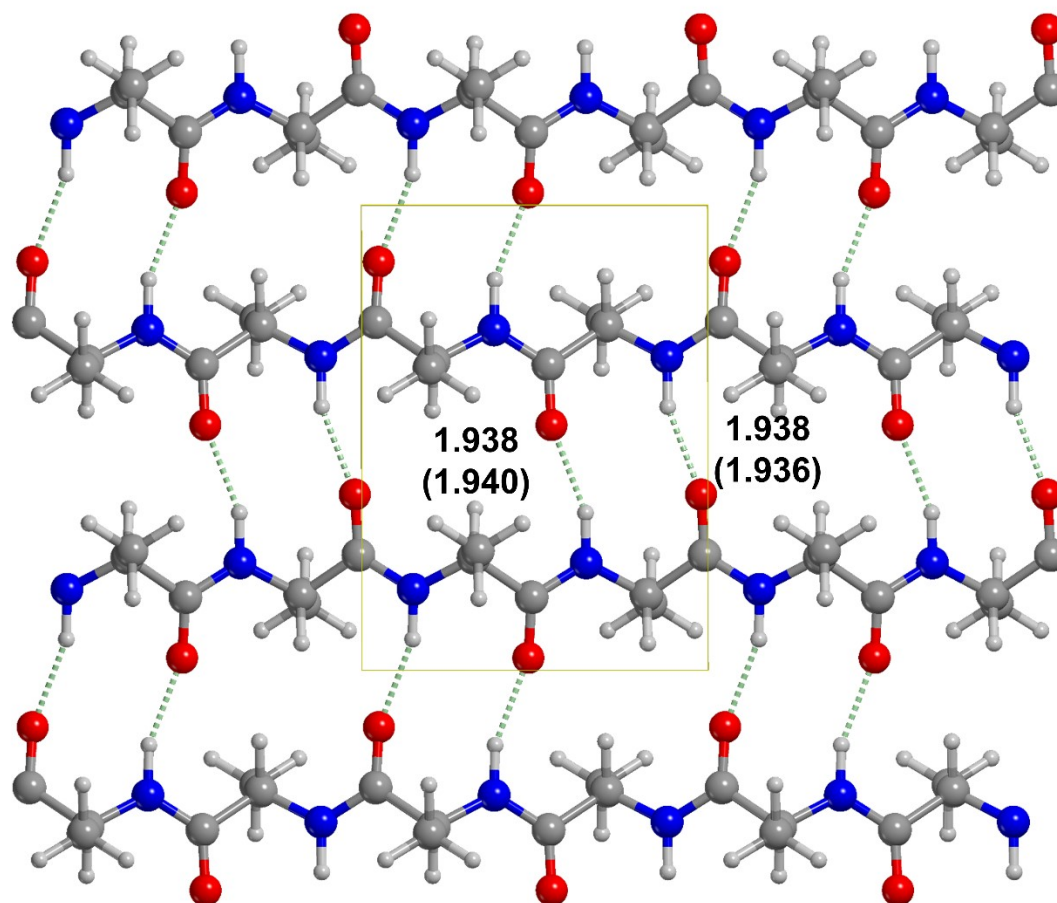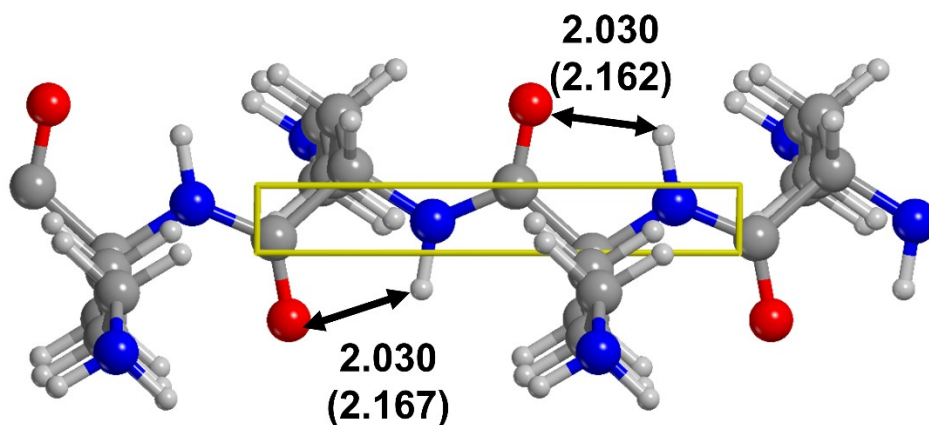
Figure S7. PBE-D2* optimized geometry for the isolated periodic antiparallel polyalanine β-sheet (ALA_β-sheet_AP). Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM. The unit cell is represented in yellow. Bond distances are in Å. Hydrogen in white, carbon in grey, oxygen in red, nitrogen in blue.
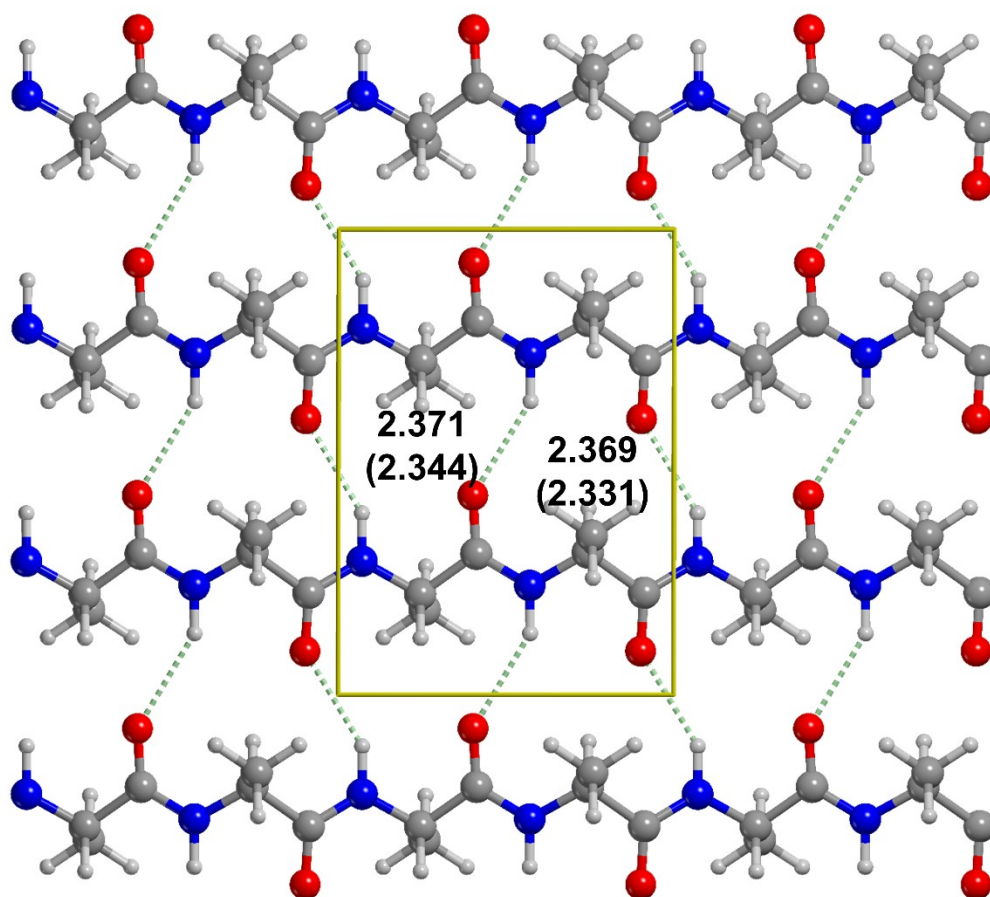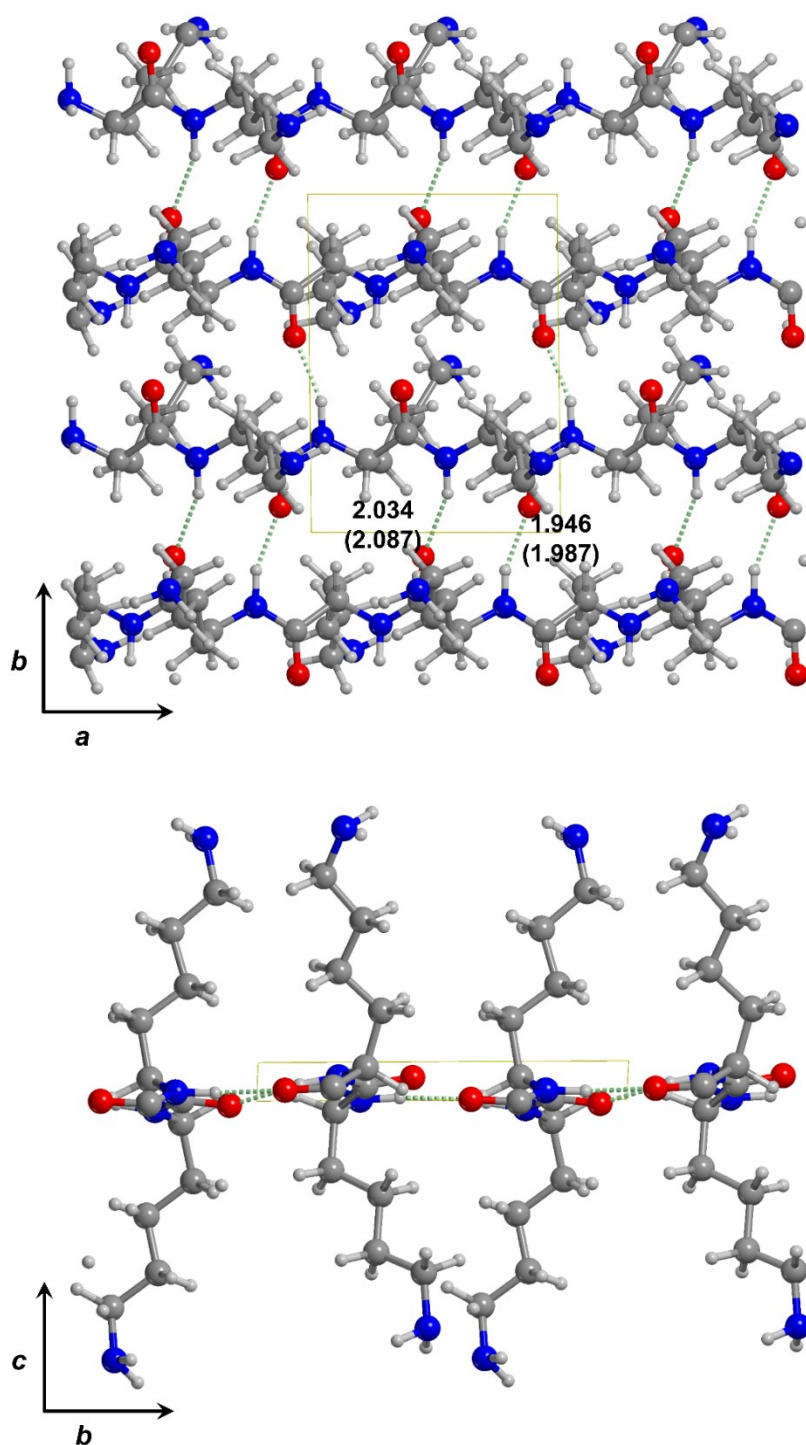
Figure S8. PBE-D2* optimized geometry for the isolated periodic parallel polyalanine β-sheet (ALA_β-sheet_P). Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM. The unit cell is represented in yellow. Bond distances are in Å. Hydrogen in white, carbon in grey, oxygen in red, nitrogen in blue.
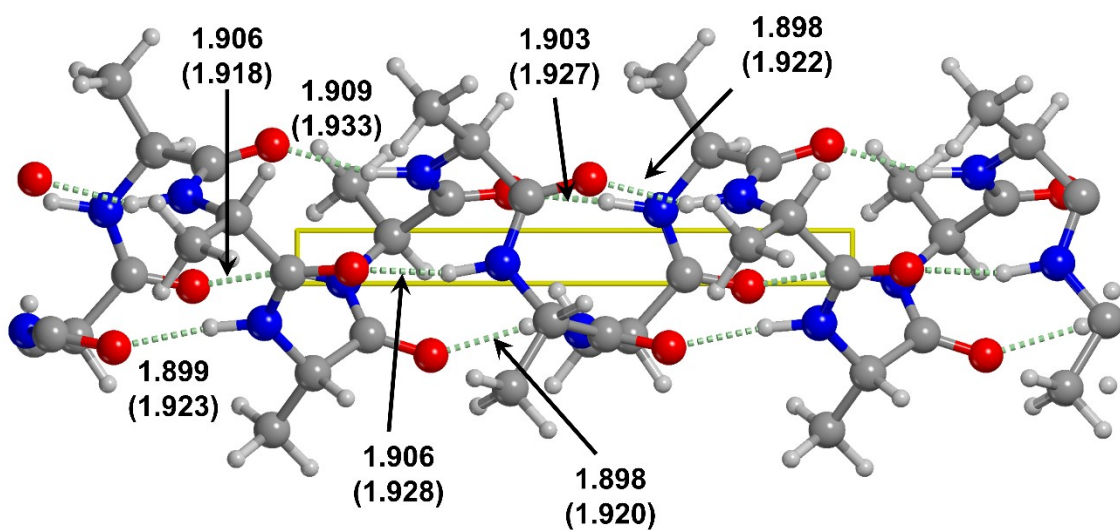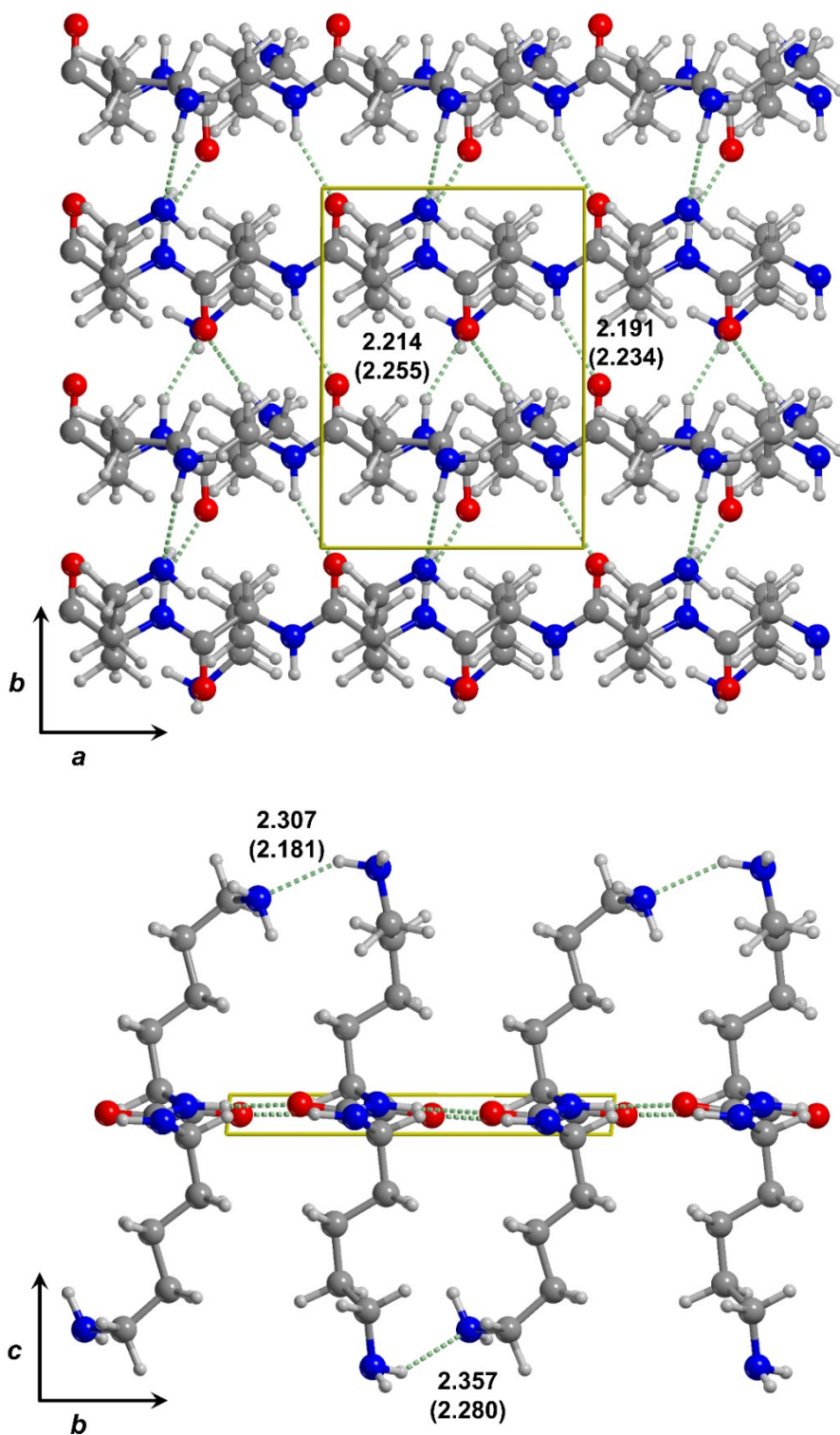
Figure S9. PBE-D2* optimized geometry for the isolated periodic polyalanine α-helix (ALA_α-helix). Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM. The unit cell is represented in yellow. Bond distances are in Å. Hydrogen in white, carbon in grey, oxygen in red, nitrogen in blue.
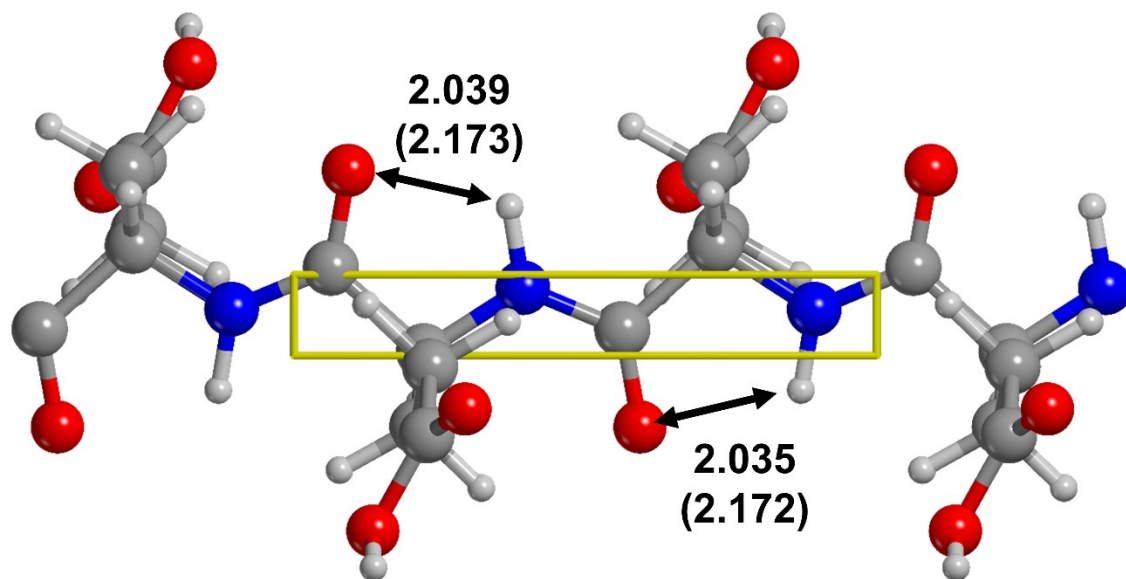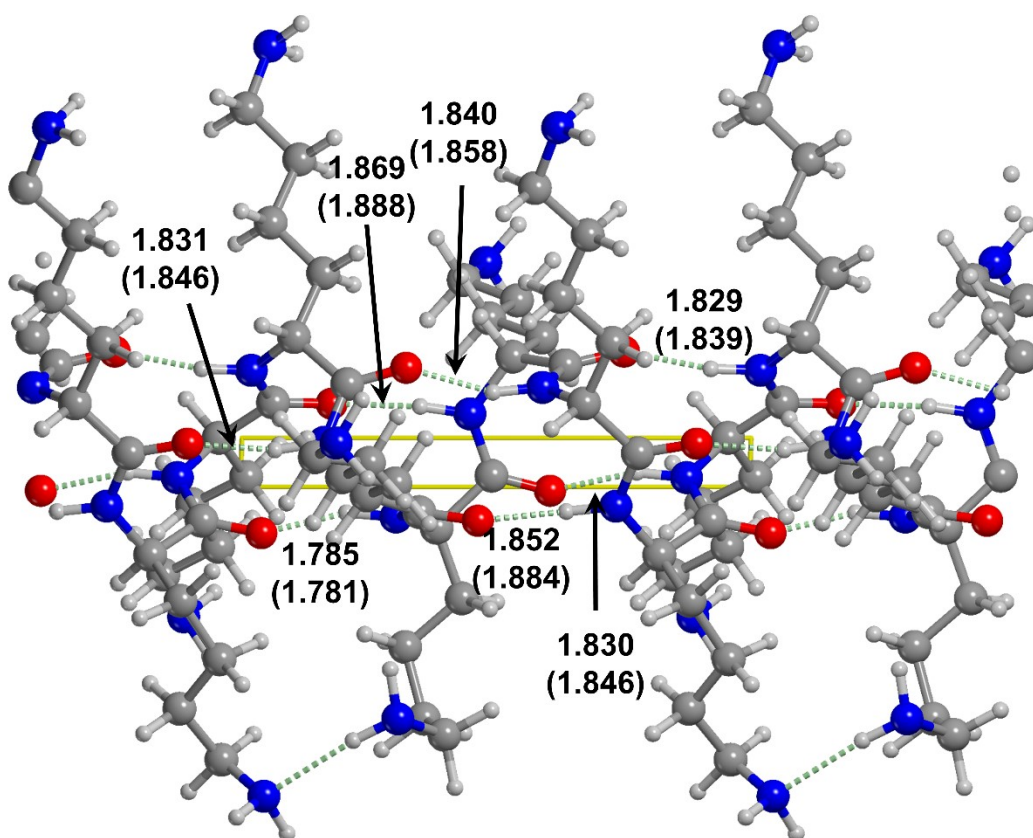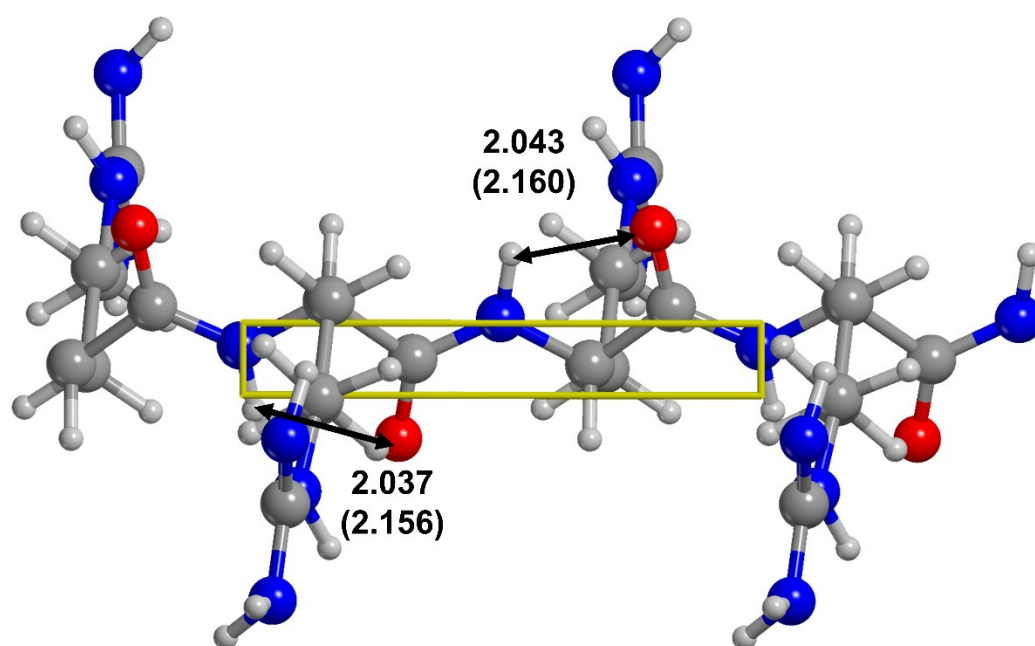
Figure S10. PBE-D2* optimized geometry for the isolated periodic linear polyglutamic acid polymer (GLU_linear). Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM. The unit cell is represented in yellow. Bond distances are in Å. Hydrogen in white, carbon in grey, oxygen in red, nitrogen in blue.

Figure S11. PBE-D2* optimized geometry for the isolated periodic antiparallel polyglutamic acid β-sheet (GLU_β-sheet_AP). Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM. The unit cell is represented in yellow. Bond distances are in Å. Hydrogen in white, carbon in grey, oxygen in red, nitrogen in blue.
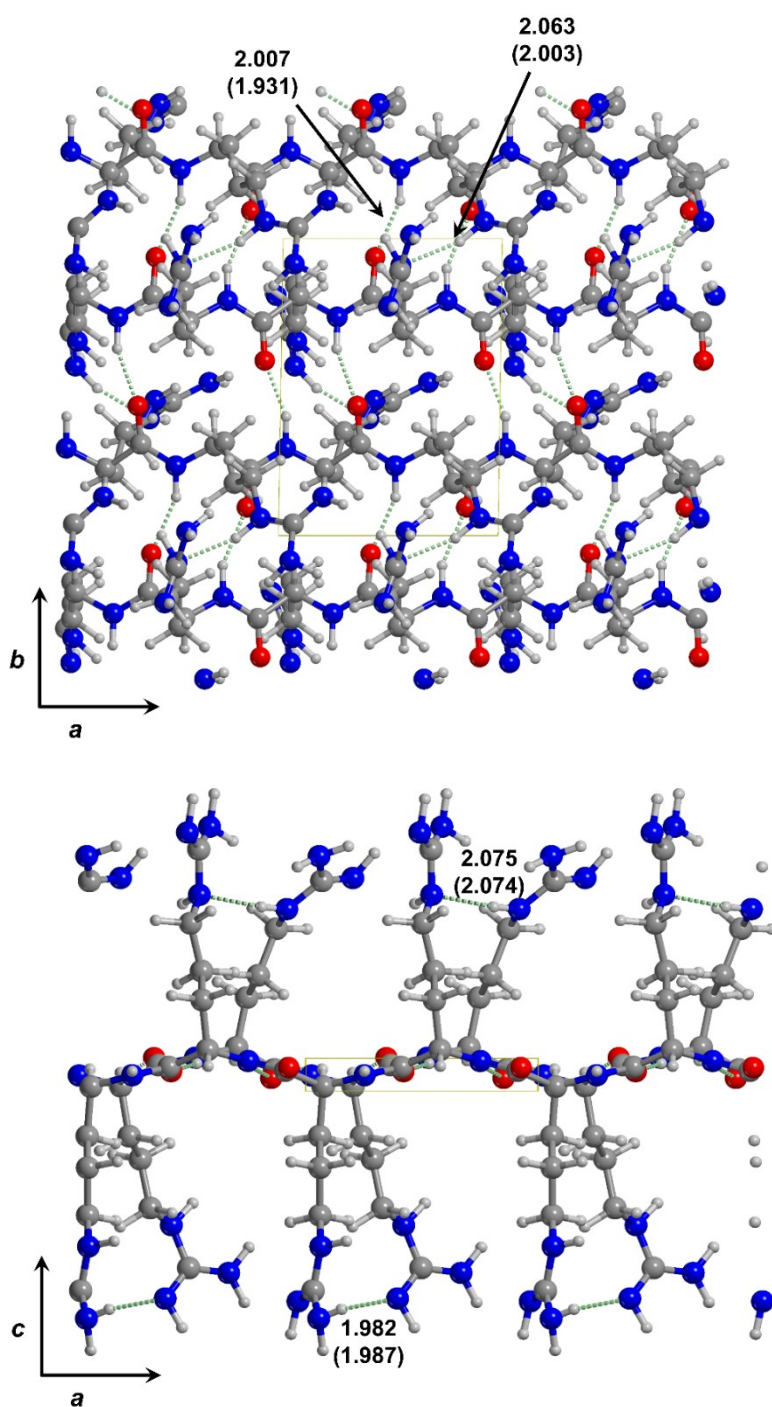
Figure S12. PBE-D2* optimized geometry for the isolated periodic parallel polyglutamic acid β-sheet (GLU_β-sheet_P). Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM. The unit cell is represented in yellow. Bond distances are in Å. Hydrogen in white, carbon in grey, oxygen in red, nitrogen in blue.
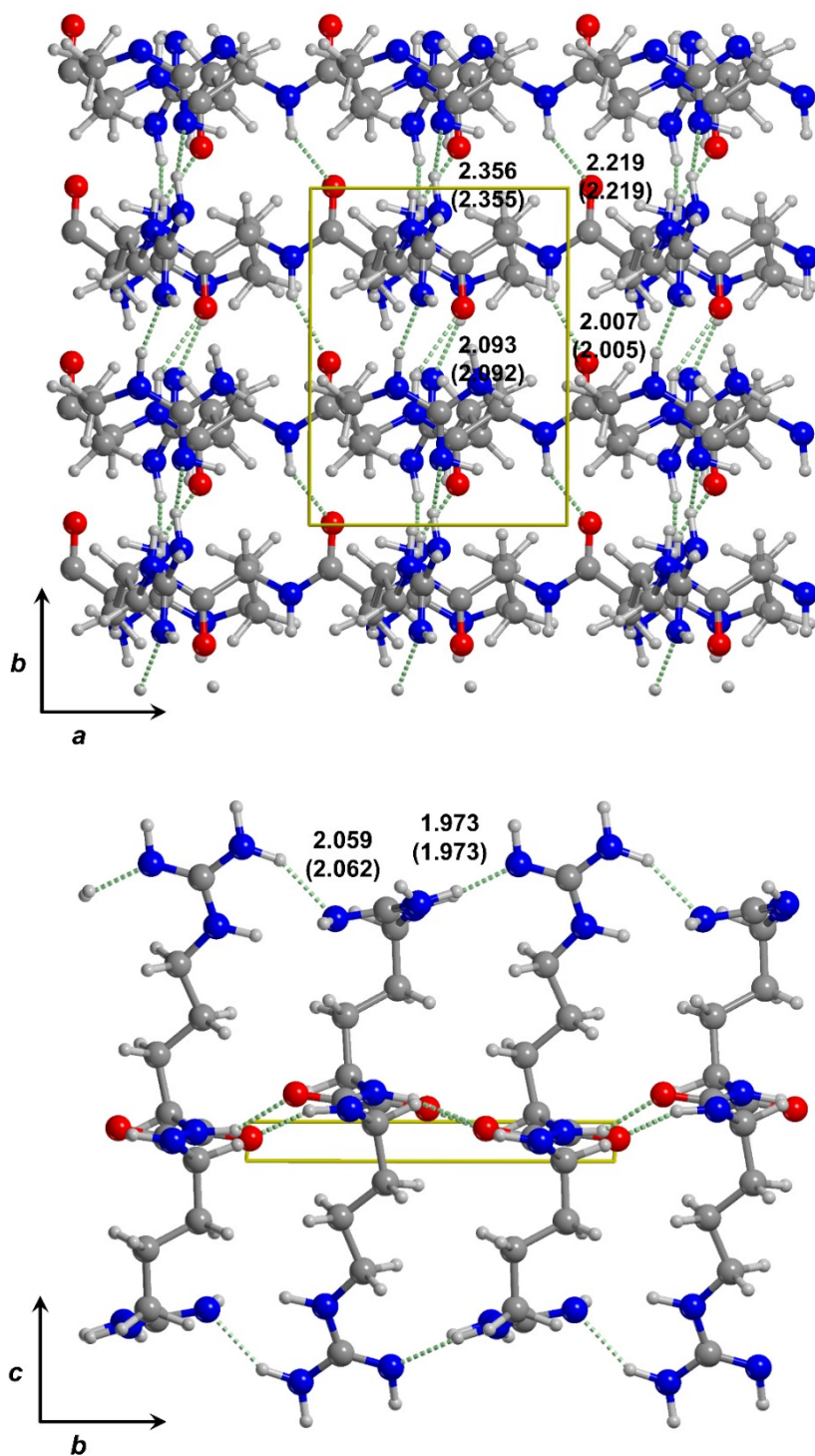
Figure S13. PBE-D2* optimized geometry for the isolated periodic polyglutamic acid α-helix (GLU_α-helix). Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM. The unit cell is represented in yellow. Bond distances are in Å. Hydrogen in white, carbon in grey, oxygen in red, nitrogen in blue.
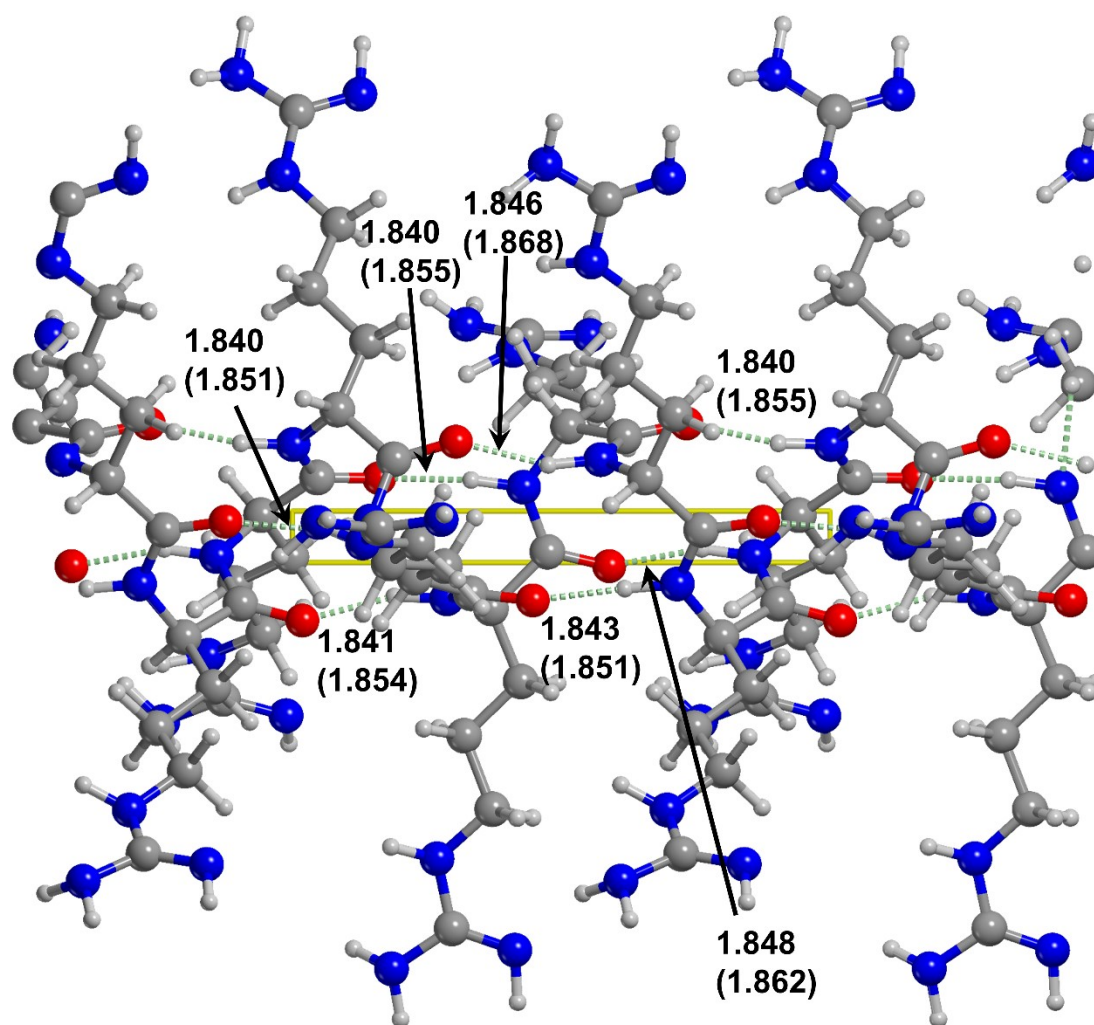
Figure S18. PBE-D2* optimized geometry for the isolated periodic linear polylysine polymer (LYS_linear). Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM. The unit cell is represented in yellow. Bond distances are in Å. Hydrogen in white, carbon in grey, oxygen in red, nitrogen in blue.

Figure S19. PBE-D2* optimized geometry for the isolated periodic parallel antipolylysine β-sheet (LYS_β-sheet_P). Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM. The unit cell is represented in yellow. Bond distances are in Å. Hydrogen in white, carbon in grey, oxygen in red, nitrogen in blue.

Figure S20. PBE-D2* optimized geometry for the isolated periodic parallel polylysine β-sheet (LYS_β-sheet_P). Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM. The unit cell is represented in yellow. Bond distances are in Å. Hydrogen in white, carbon in grey, oxygen in red, nitrogen in blue.

Figure S21. PBE-D2* optimized geometry for the isolated periodic polylysine α-helix. The unit cell is represented in yellow (LYS_α-helix). Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM. Bond distances are in Å. Hydrogen in white, carbon in grey, oxygen in red, nitrogen in blue.

Figure S14. PBE-D2* optimized geometry for the isolated periodic linear polyarginine polymer (ARG_linear). Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM. The unit cell is represented in yellow. Bond distances are in Å. Hydrogen in white, carbon in grey, oxygen in red, nitrogen in blue.

Figure S15. PBE-D2* optimized geometry for the isolated periodic antiparallel polyarginine β-sheet (ARG_β-sheet_AP). Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM. The unit cell is represented in yellow. Bond distances are in Å. Hydrogen in white, carbon in grey, oxygen in red, nitrogen in blue.

Figure S16. PBE-D2* optimized geometry for the isolated periodic parallel polyarginine β-sheet (ARG_β-sheet_P). Bare values refer to distances for optimized structures in the gas phase, while the 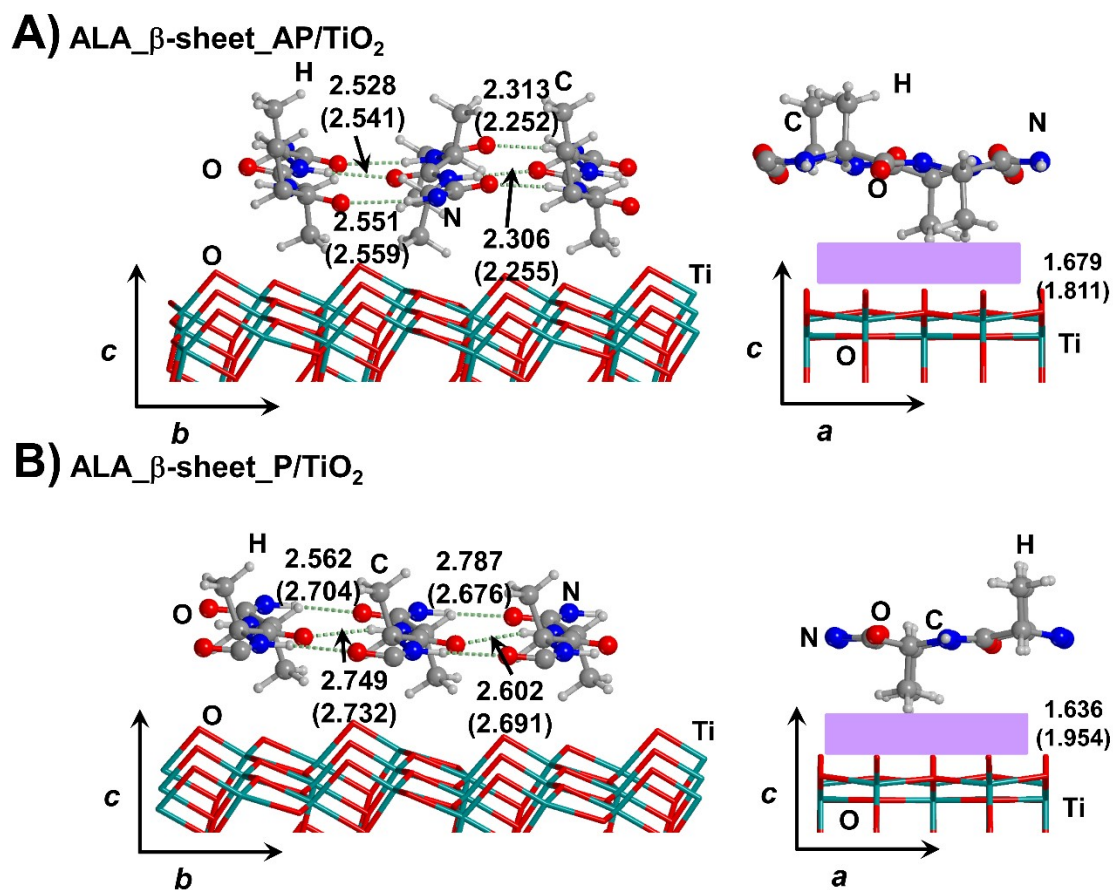values in parenthesis are for those optimized with the PCM. The unit cell is represented in yellow. Bond distances are in Å. Hydrogen in white, carbon in grey, oxygen in red, nitrogen in blue.

Figure S17. PBE-D2* optimized geometry for the isolated periodic polyarginine α-helix (ARG_α-helix). Bare values refer to distances for optimized structures in the gas phase, while the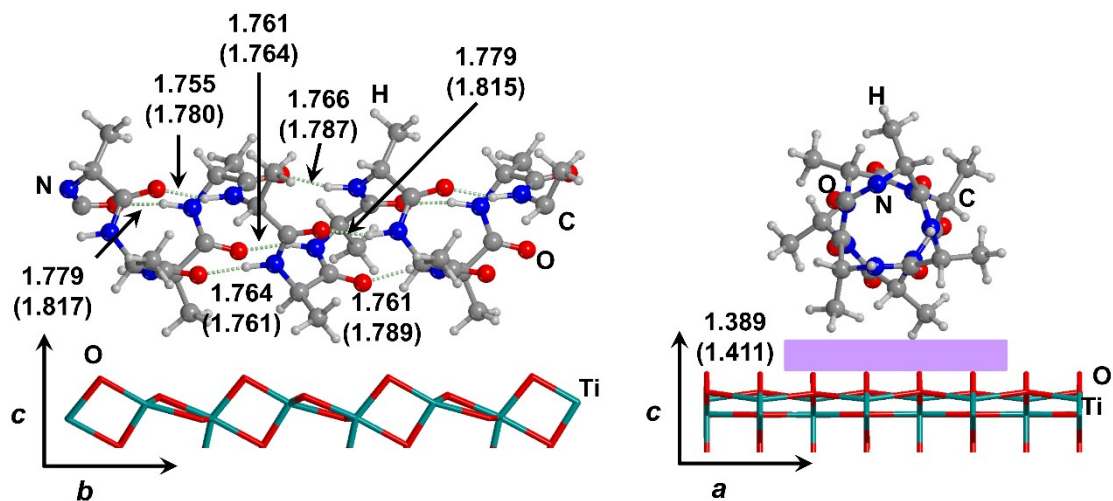 values in parenthesis are for those optimized with the PCM. The unit cell is represented in yellow. Bond distances are in Å. Hydrogen in white, carbon in grey, oxygen in red, nitrogen in blue.
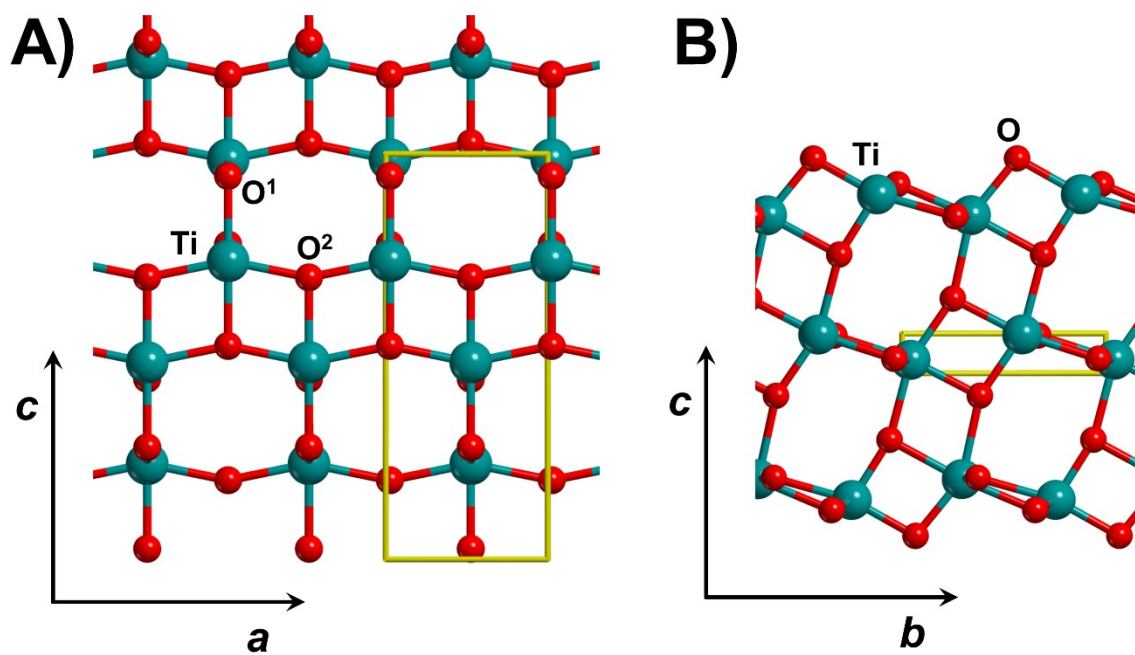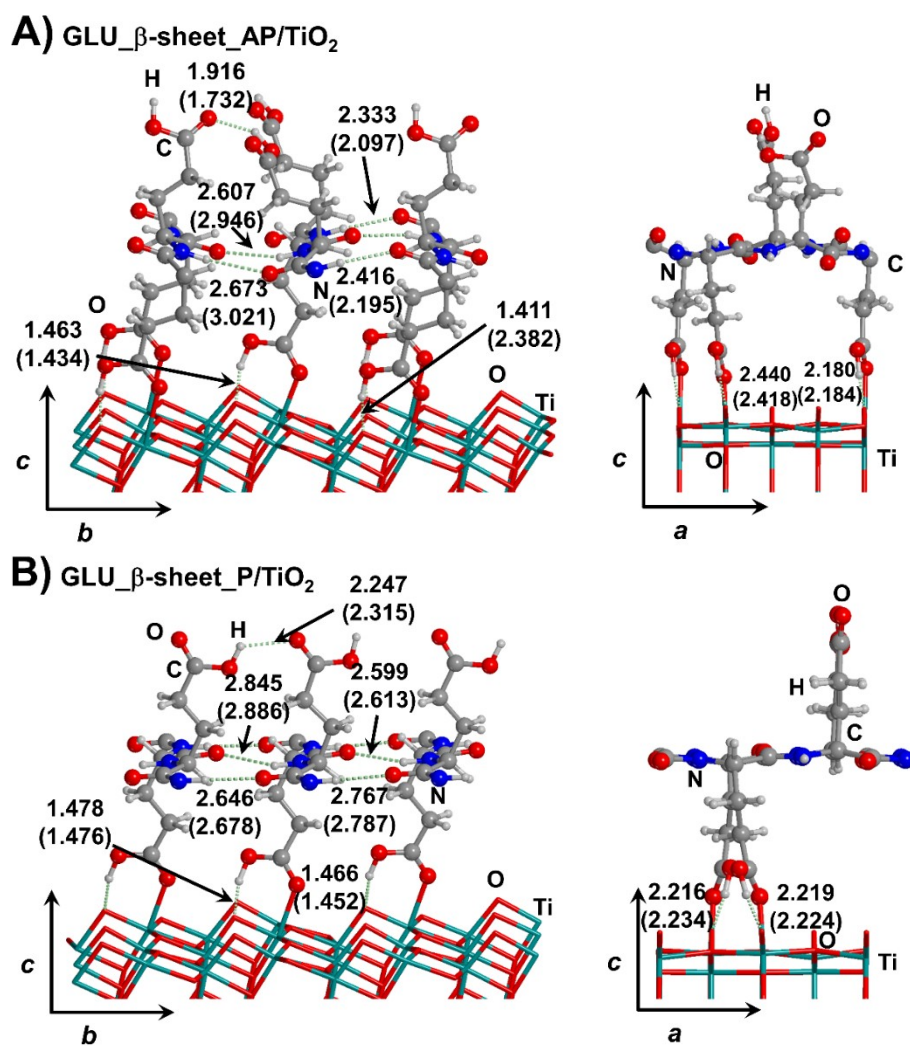
Figure S18. PBE-D2* optimized structure of: A) bulk anatase, and B) the (101) anatase surface viewed along the *a* direction.

A) GLY_linear/TiO$_2$
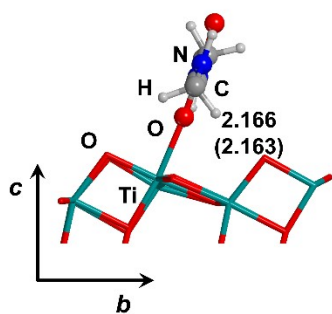
B) GLY_β-sheet_AP/TiO$_2$
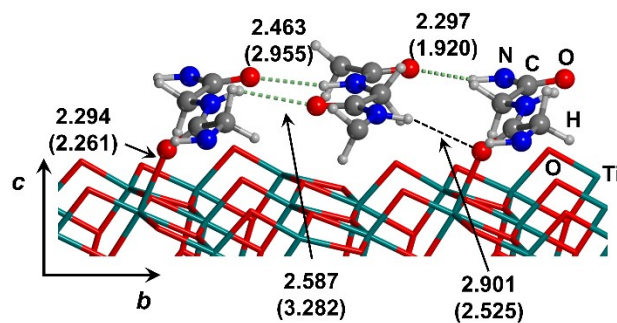
C) GLY_β-sheet_P/TiO$_2$
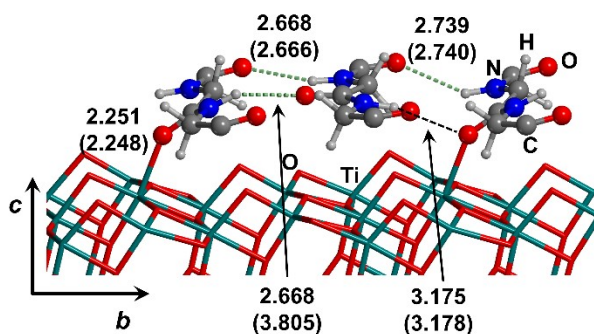
D) GLY_α-helix_2/TiO$_2$
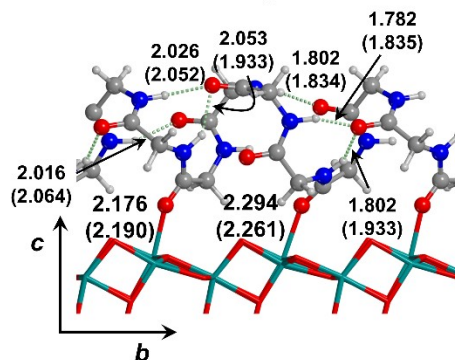
Figure S19. PBE-D2* optimized structures of extended polyglycine (A), antiparallel (B) and parallel polyglycine β-sheets, and polyglycine α-helix (D) adsorbed on the TiO$_2$ (101) anatase surface. Numbers in parenthesis refers to values in gas phase, while number without parenthesis refers to values with implicit solvation.
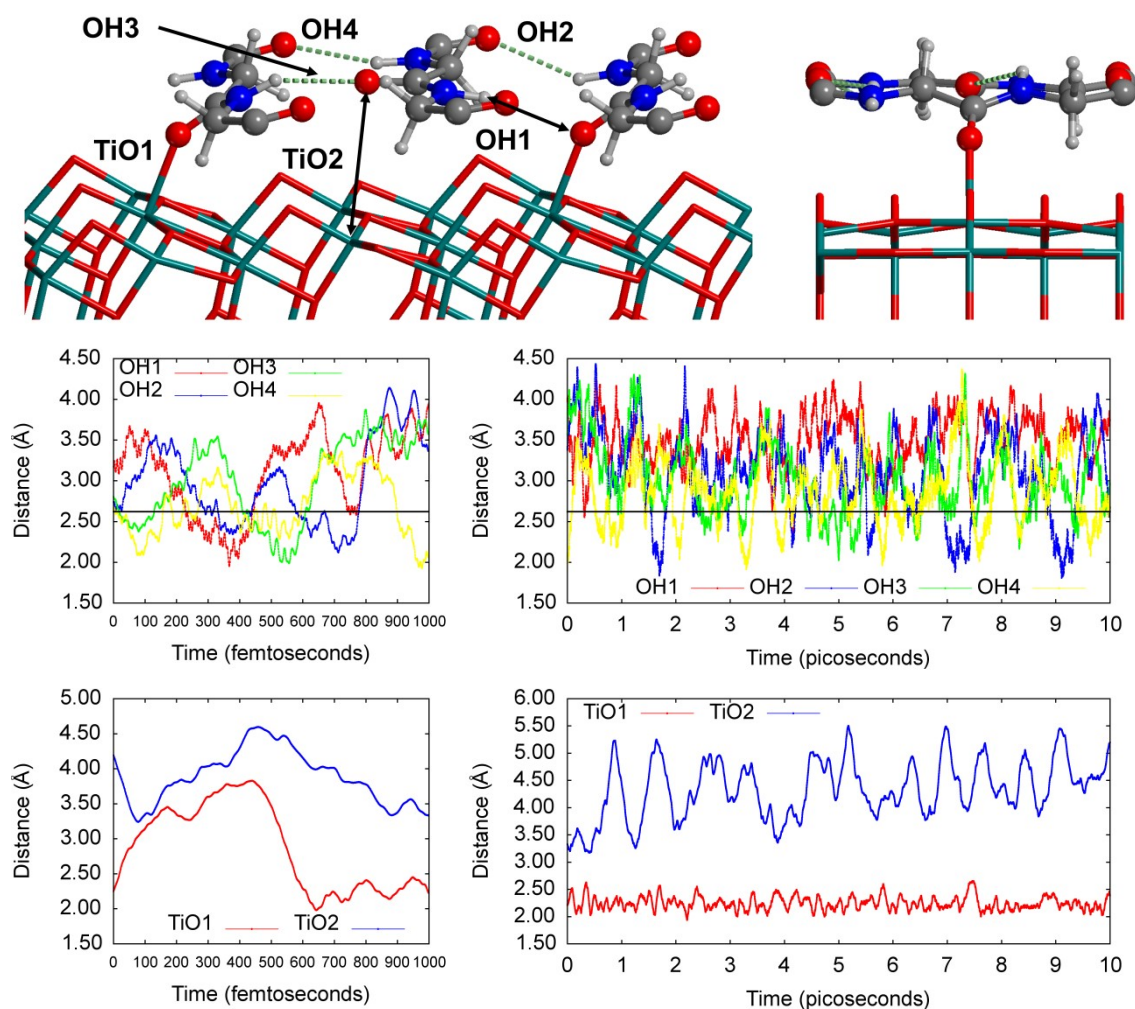
Figure S20. PBE-D2* optimized geometry for the β-sheets_P/TiO$_2$ (top). Evolution of the H-bond pattern (middle) and of Ti—O distances (bottom) during the MD simulation in both its equilibration (left part) and production (right part) period. Hydrogen in white, carbon in grey, oxygen in red, nitrogen in blue, titanium in cyan.
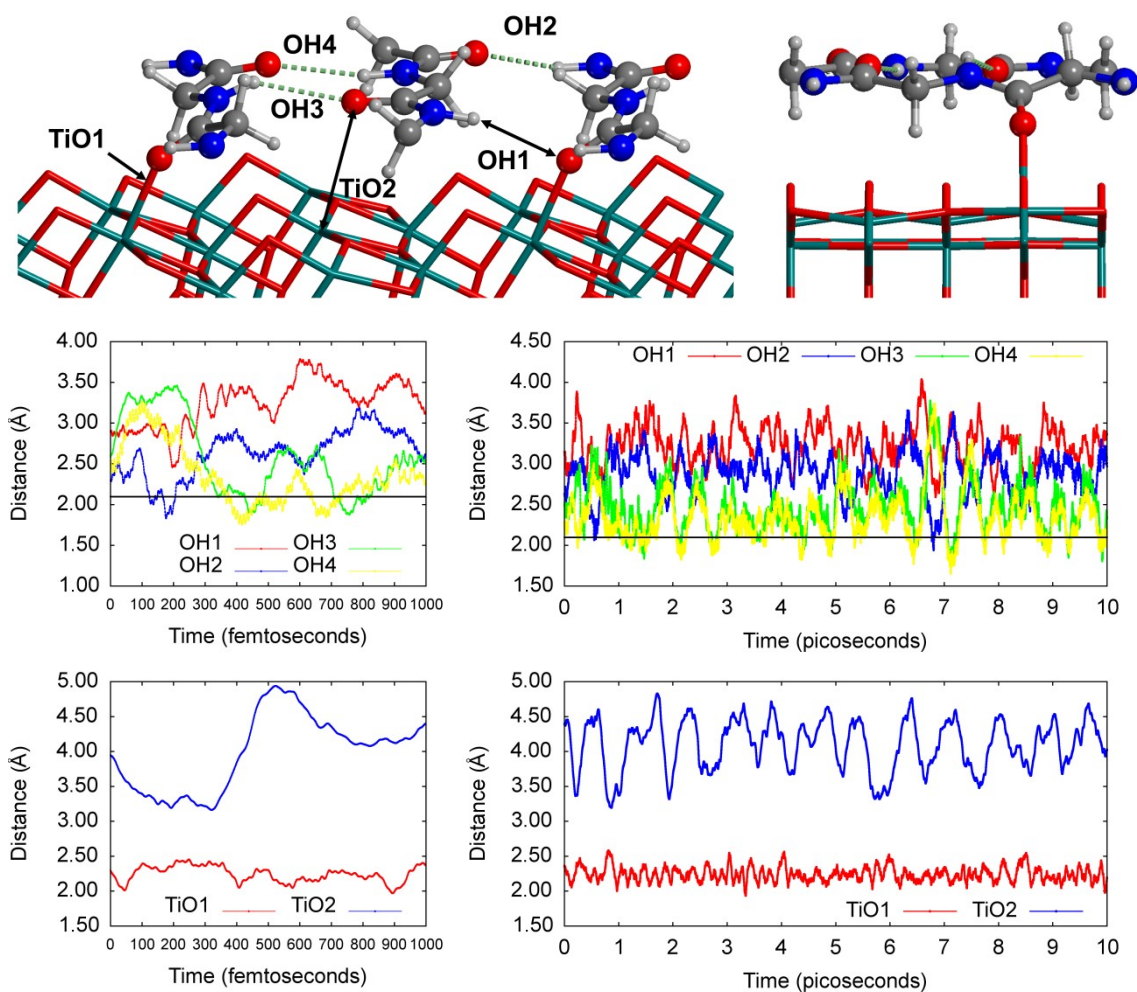
Figure S21. PBE-D2* optimized geometry for the β-sheets_AP/TiO₂ complex (top). Evolution of the H-bond pattern (middle) and of Ti—O distances (bottom) during the MD simulation in both its equilibration (left part) and production (right part) period. Hydrogen in white, carbon in grey, oxygen in red, nitrogen in blue, titanium in cyan.
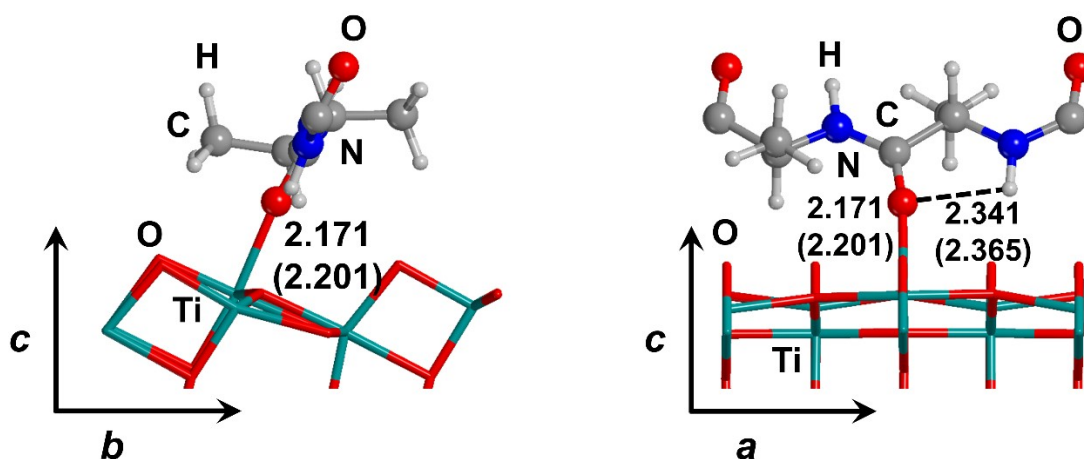
Figure S22. PBE-D2* optimized structure of the ALA_linear/TiO$_2$ complex. Bond distances are in Å. Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM.
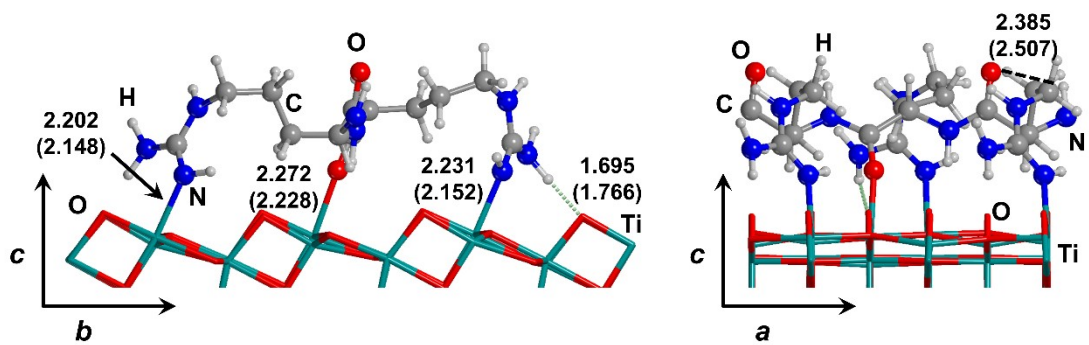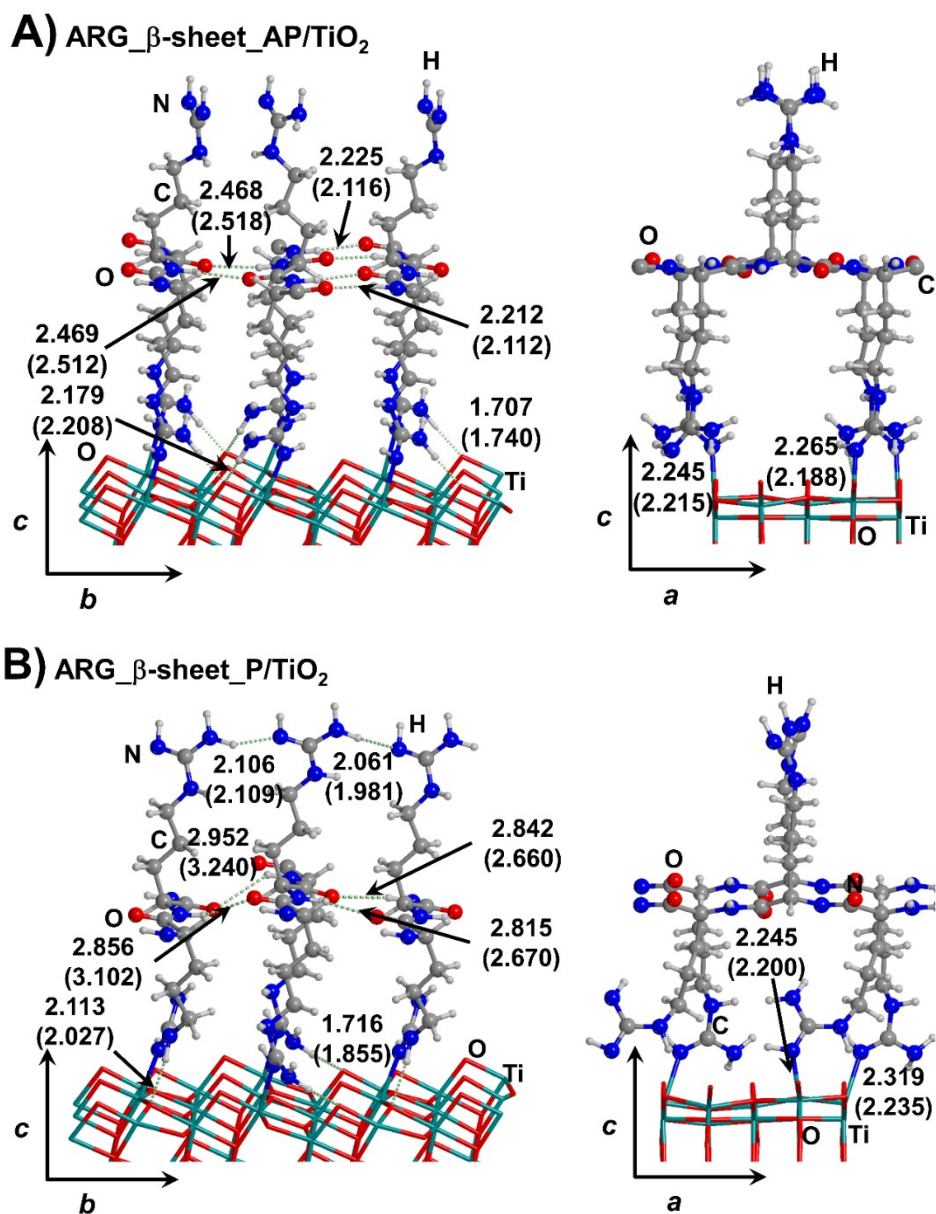
A) ALA_β-sheet_AP/TiO₂

B) ALA_β-sheet_P/TiO₂

Figure S23. PBE-D2* optimized structures of the ALA_β-sheet_AP/TiO₂ (A) and ALA_β-sheet_P/TiO₂ (B) complexes. Bond distances are in Å. Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM.
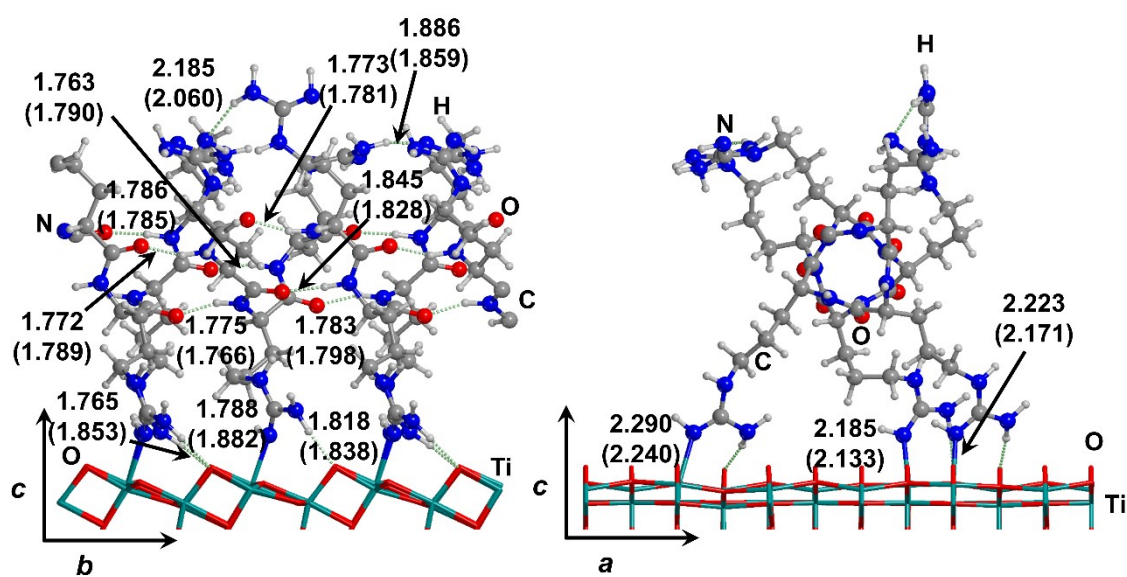
Figure S24. PBE-D2* optimized structure of the ALA_α-helix/TiO$_2$ complex. Bond distances are in Å. Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM.
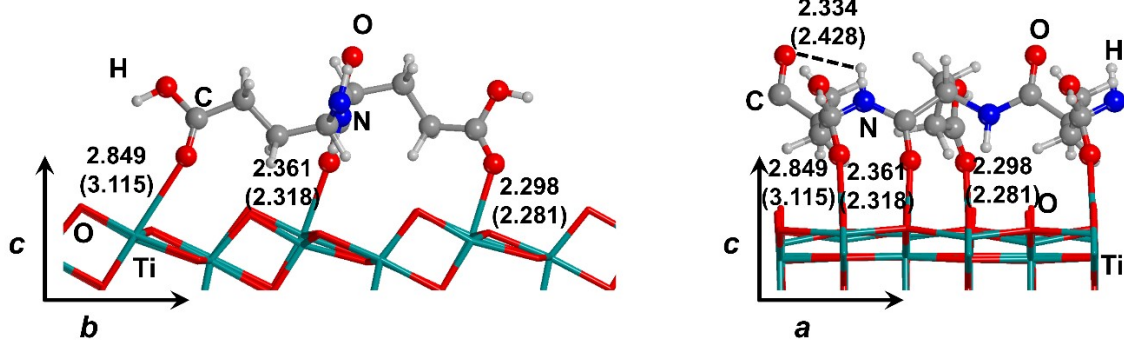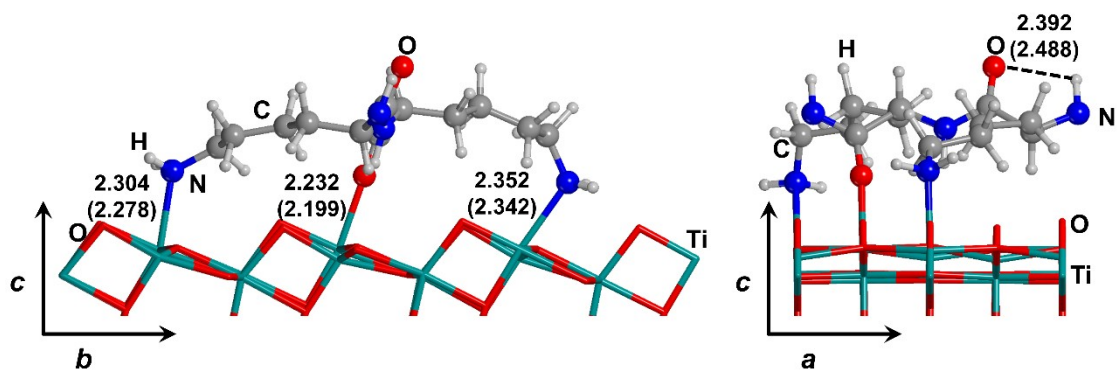
Figure S25. PBE-D2* optimized structure of the GLU_linear/TiO$_2$ complex. Bond distances are in Å. Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM.
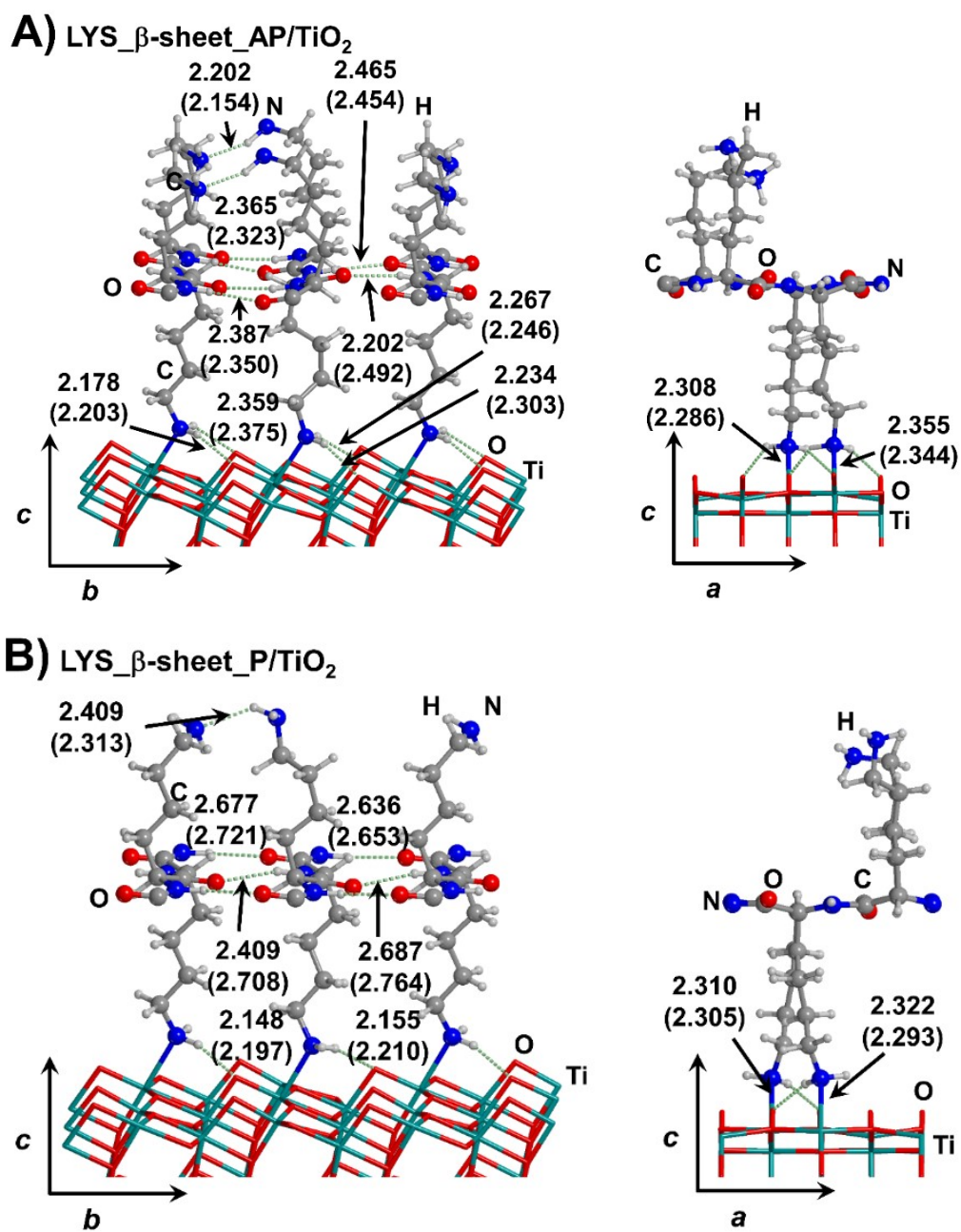
Figure S26. PBE-D2* optimized structures of the GLU_β-sheet_AP/TiO$_2$ (A) and GLU_β-sheet_P/TiO$_2$ (B) complexes. Bond distances are in Å. Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM.
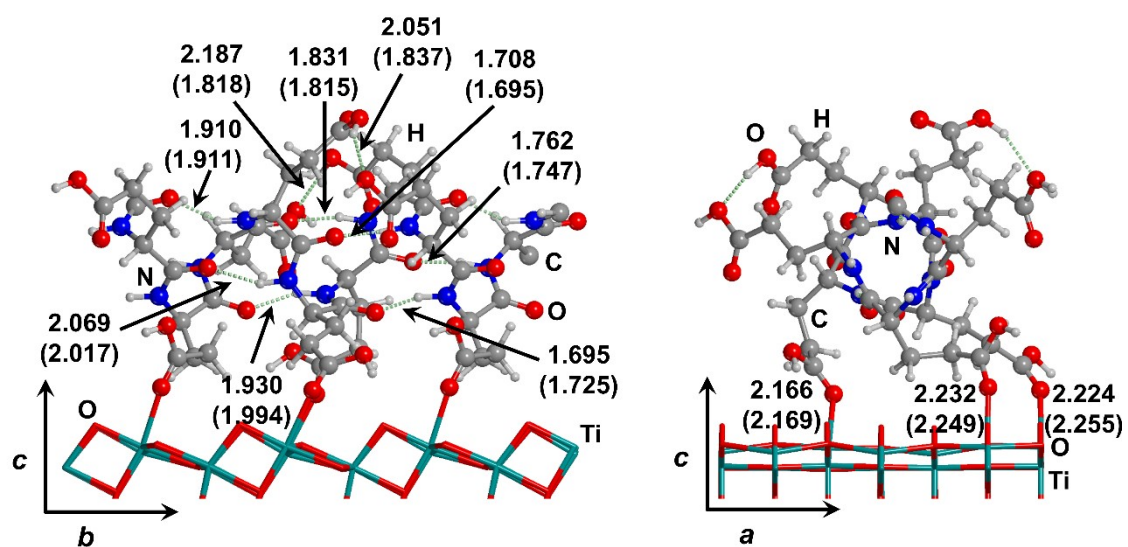
Figure S27. PBE-D2* optimized structure of the GLU_α-helix/TiO$_2$ complex. Bond distances are in Å. Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM.
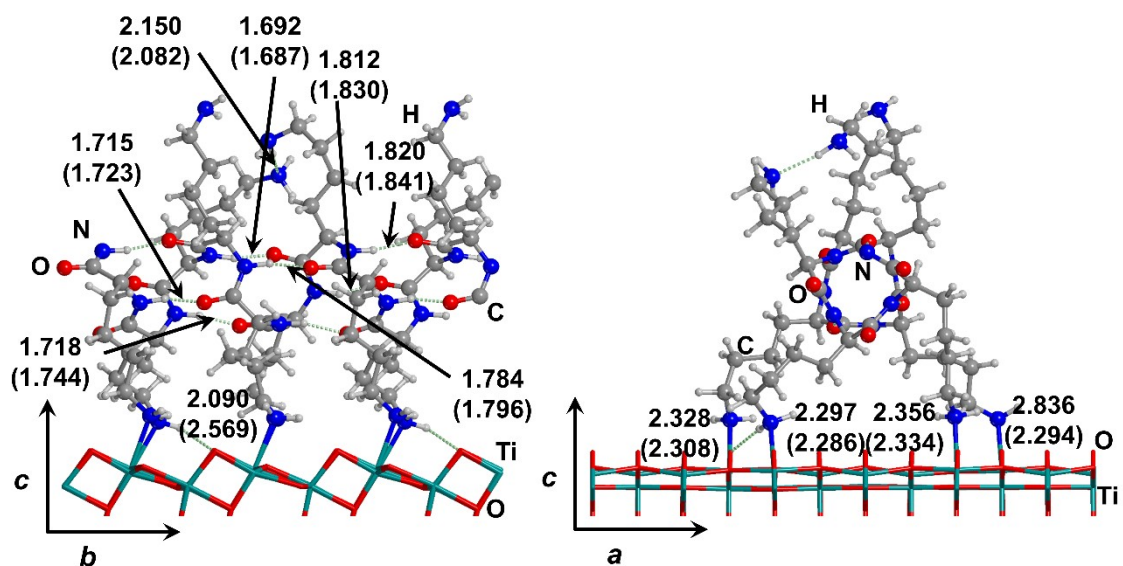
Figure S28. PBE-D2* optimized structure of the ARG_linear/TiO$_2$ complex. Bond distances are in Å. Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM.

Figure S29. PBE-D2* optimized structures of the ARG_β-sheet_AP/TiO$_2$ (A) and ARG_β-sheet_P/TiO$_2$ (B) complexes. Bond distances are in Å. Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM.

Figure S30. PBE-D2* optimized structure of the ARG_α-helix/TiO$_2$ complex. Bond distances are in Å. Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM.

Figure S31. PBE-D2* optimized structure of the LYS_linear/TiO$_2$ complex. Bond distances are in Å. Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM.

Figure S32. PBE-D2* optimized structures of the LYS_β-sheet_AP/TiO$_2$ (A) and LYS_β-sheet_P/TiO$_2$ (B) complexes. Bond distances are in Å. Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM.

Figure S33. PBE-D2* optimized structure of the LYS_α-helix/TiO$_2$ complex. Bond distances are in Å. Bare values refer to distances for optimized structures in the gas phase, while the values in parenthesis are for those optimized with the PCM.

H-bond analysis

In the following, a detailed H-bond analysis will be presented, highlighting the differences between the polyamino acidic systems in the gas and adsorbed on the TiO_2 (101) anatase surface.

GLY - polymer

ALA - polymer
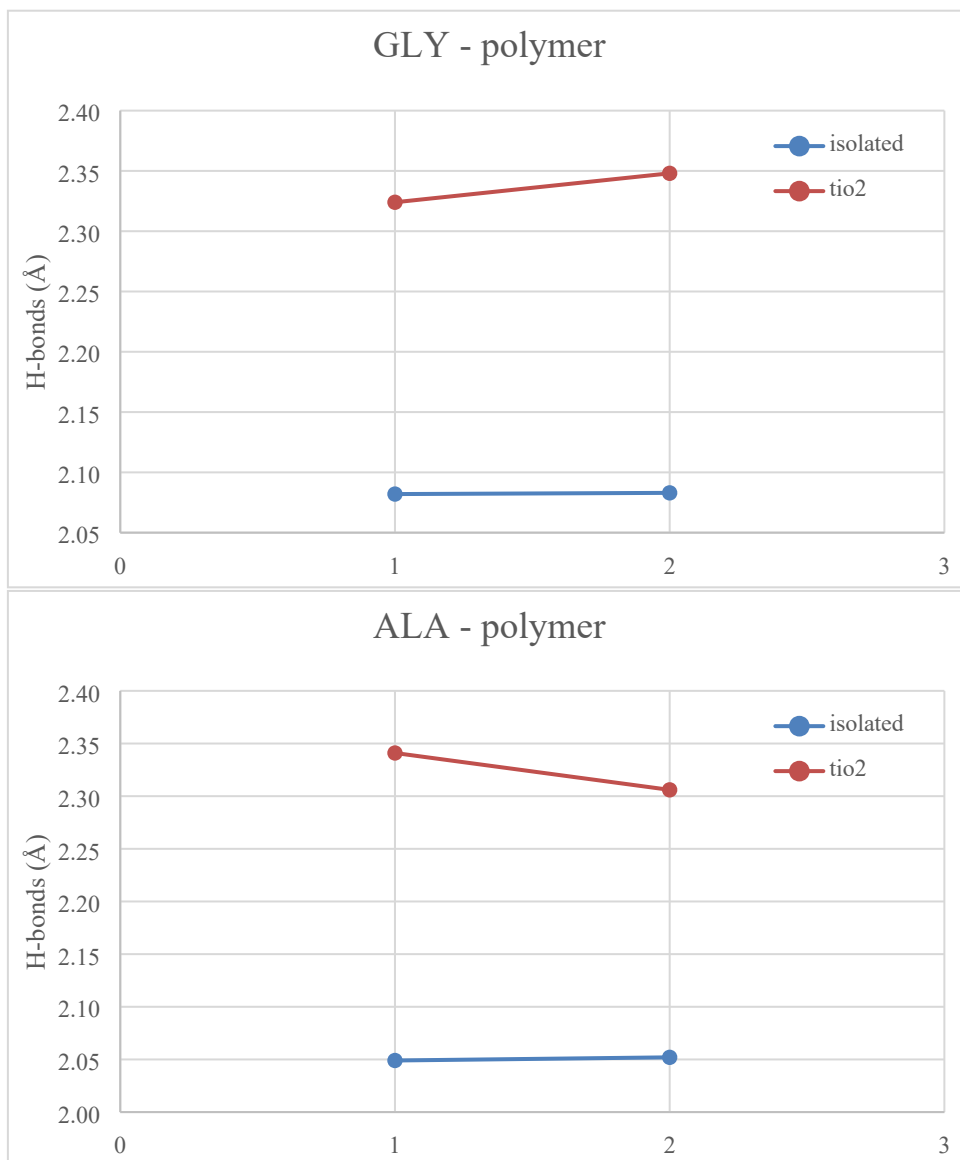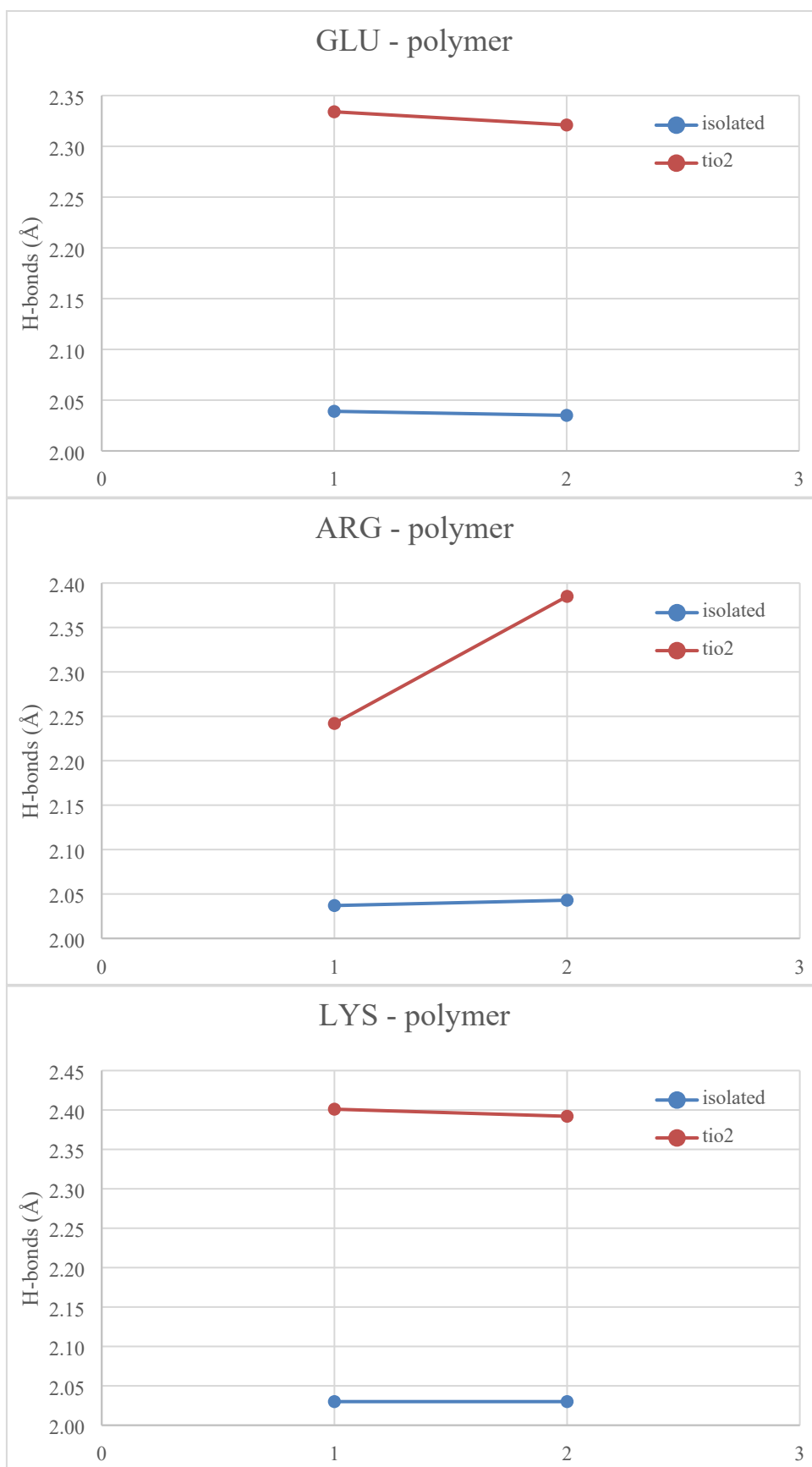
Figure S34. Comparison of the intrastrand (pseudo-) H-bonds between the polyamino acidic polymers in the gas phase (blue lines) and adsorbed on the TiO$_2$ surface (red lines).
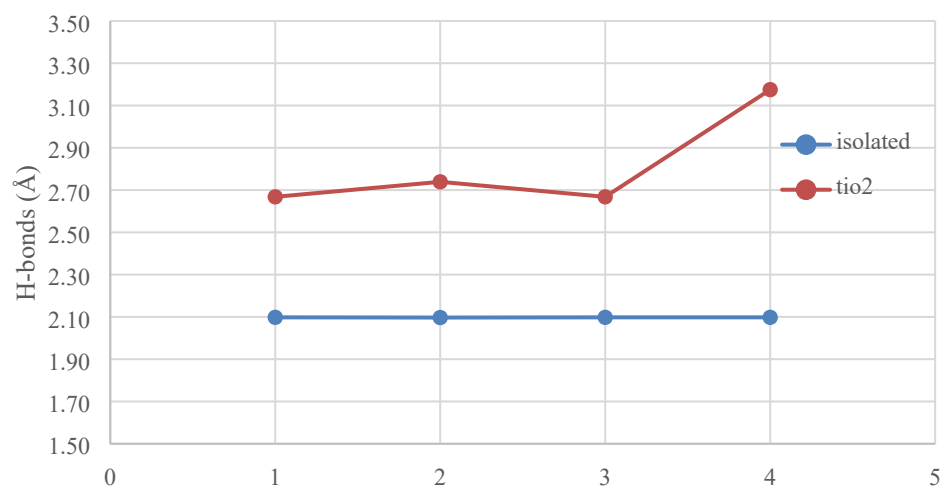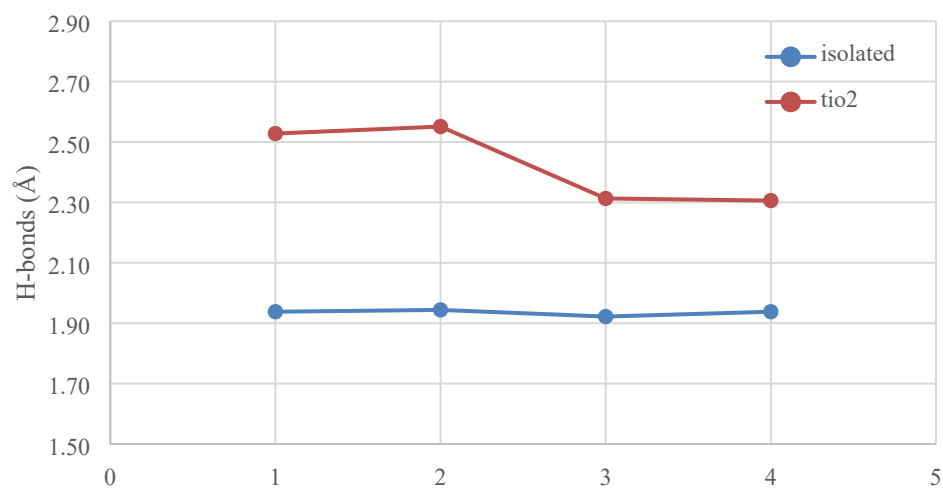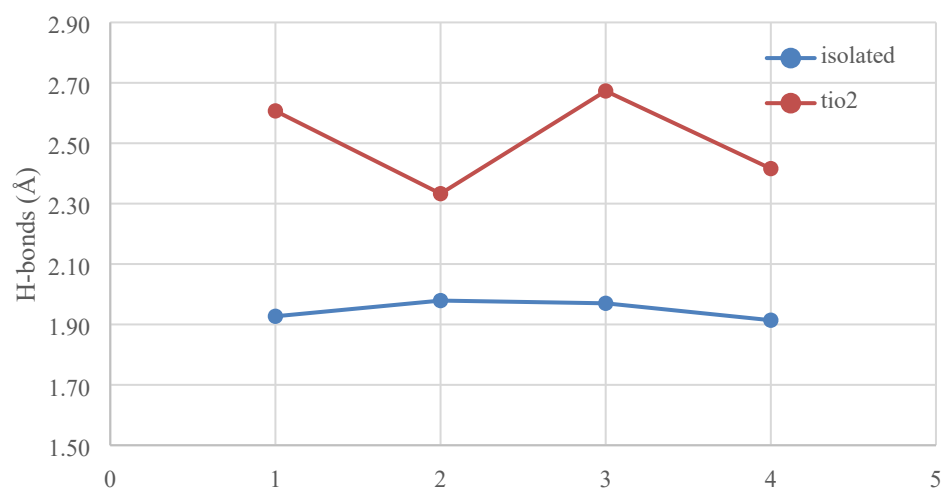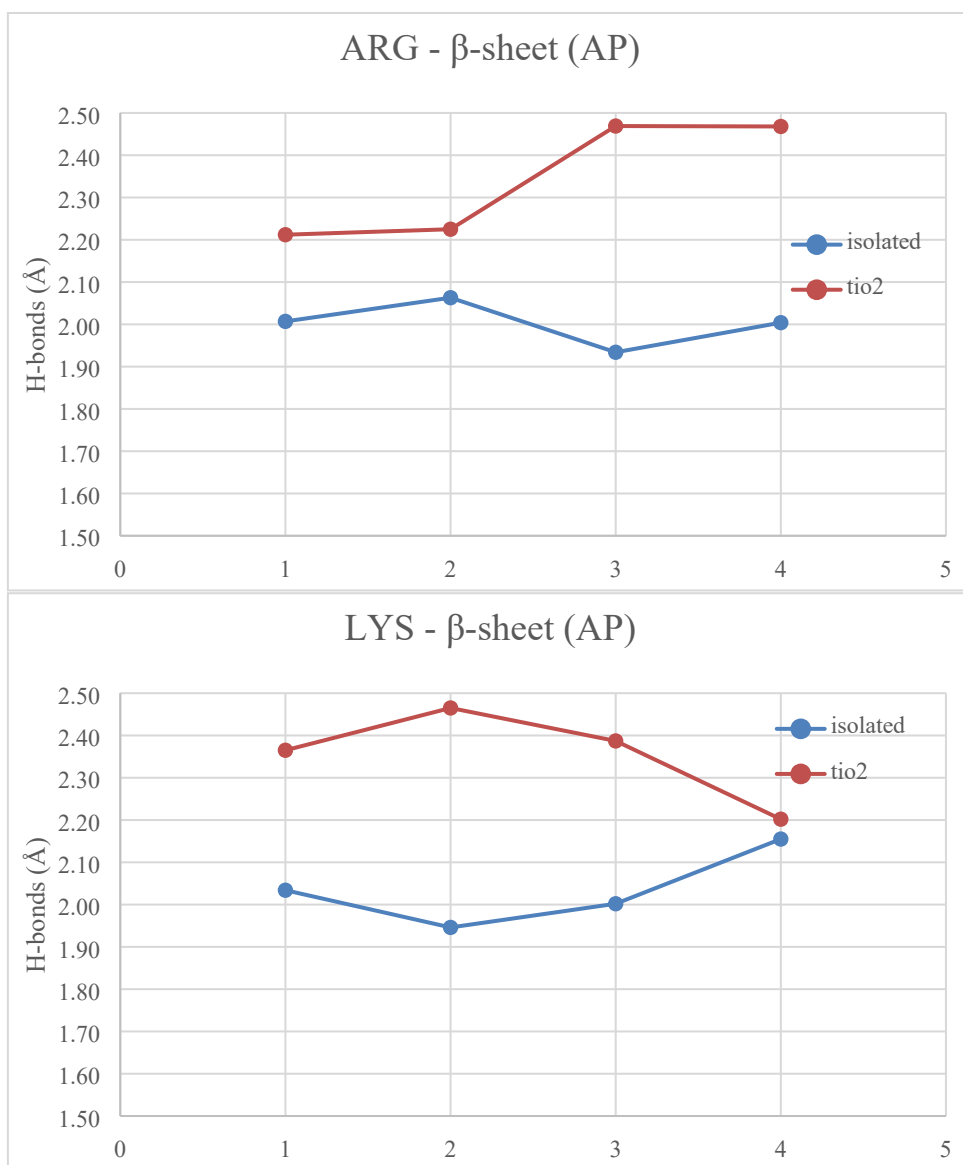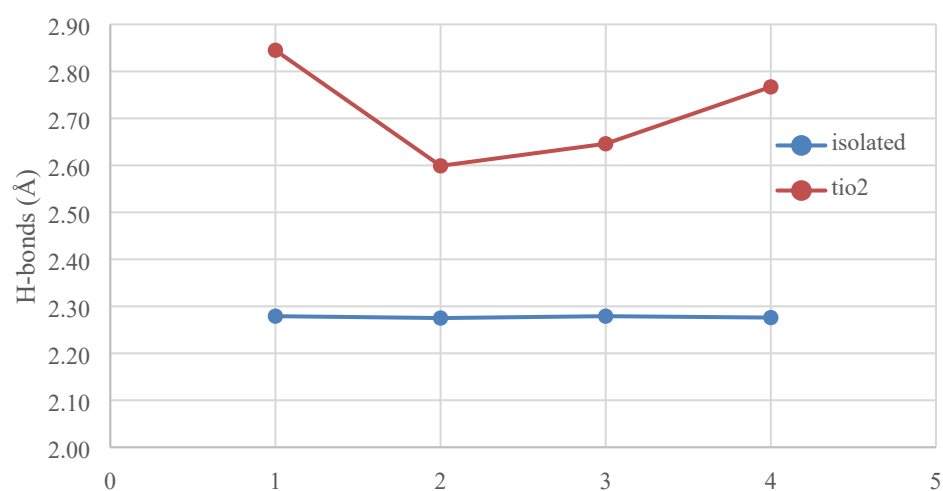
Figure S35. Comparison of the interstrand H-bonds between the polyamino acidic antiparallel (AP) β-sheets in the gas phase (blue lines) and adsorbed on the TiO$_2$ surface (red lines).
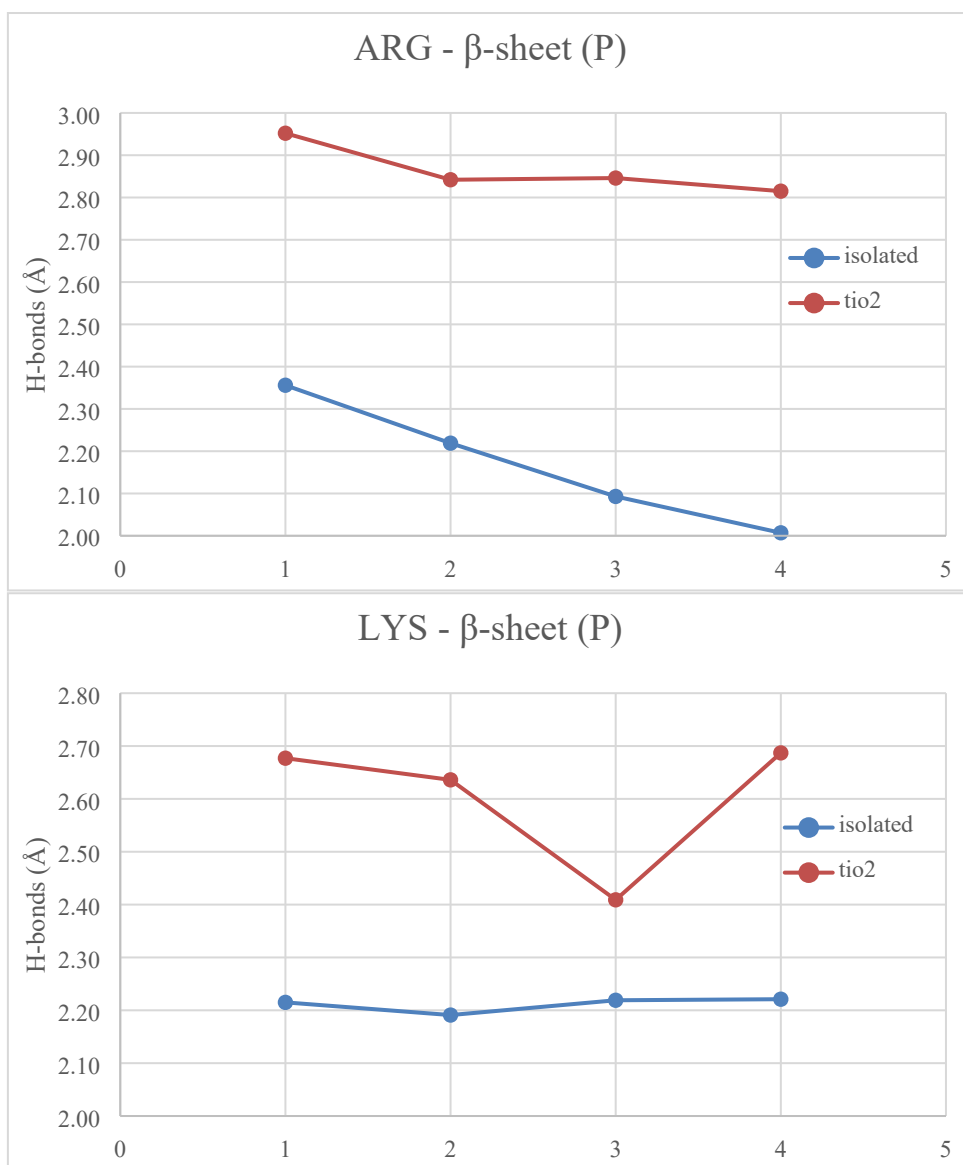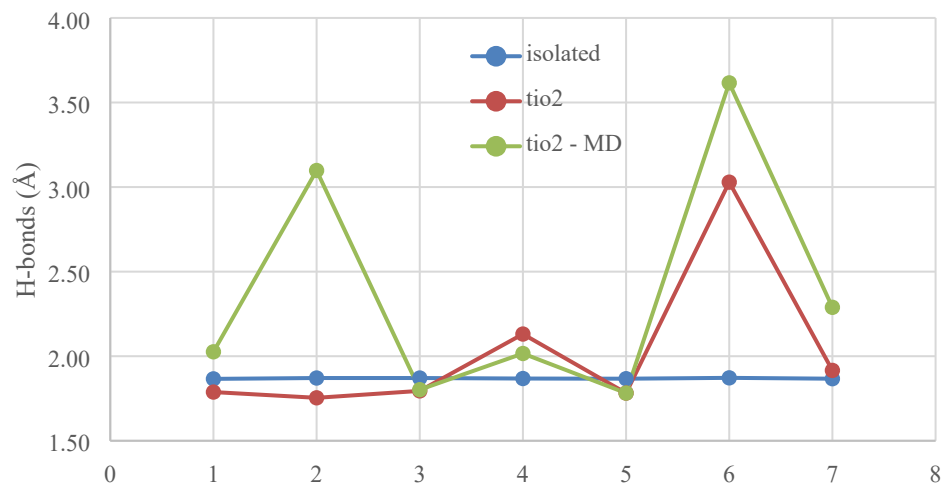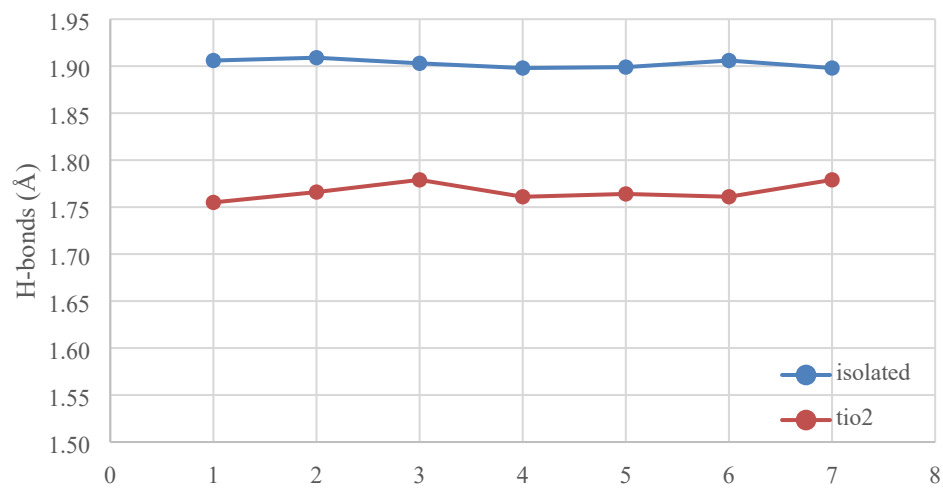
GLY - β-sheet (P)

ALA - β-sheet (P)
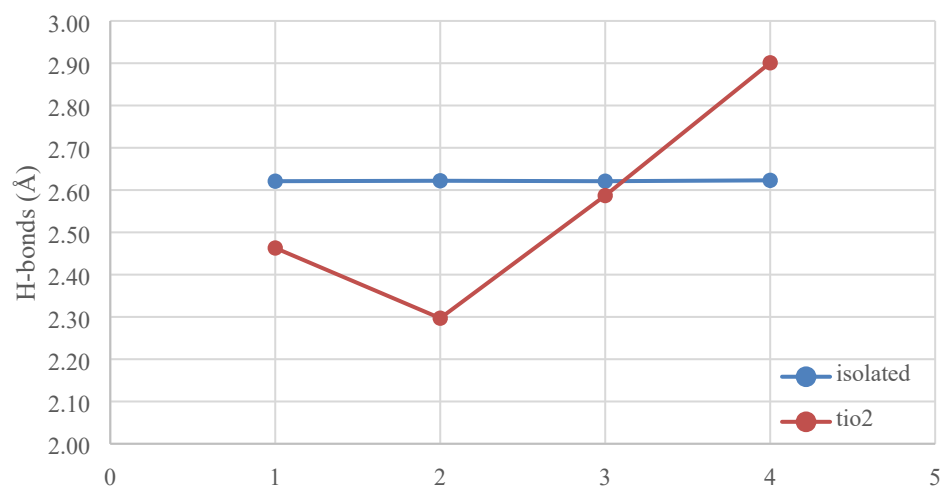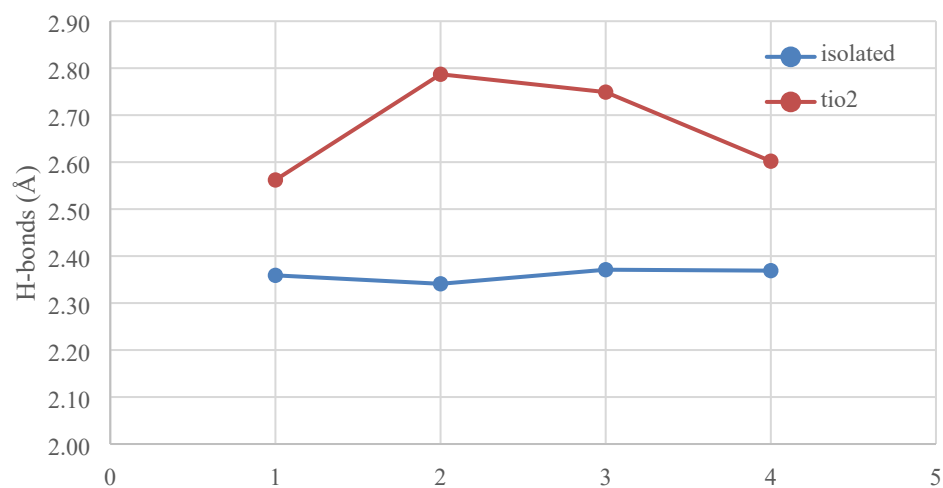
GLU - β-sheet (P)

Figure S36. Comparison of the interstrand H-bonds between the polyamino acidic parallel (P) β-sheets in the gas phase (blue lines) and adsorbed on the TiO$_2$ surface (red lines).
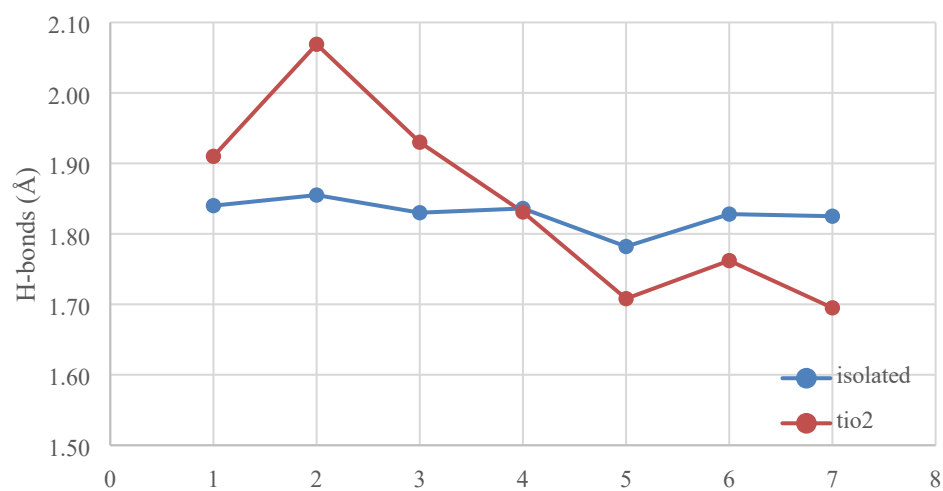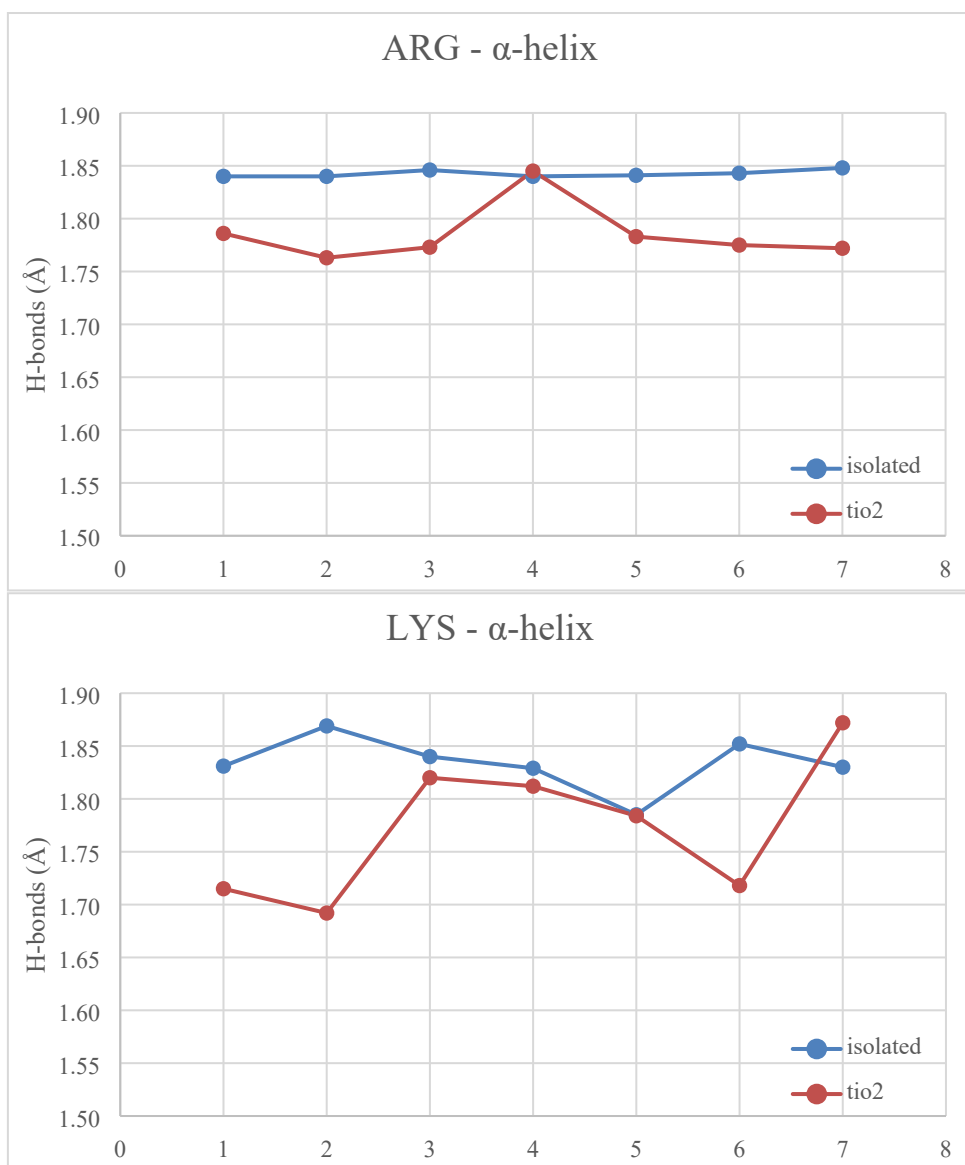
Figure S37. Comparison of the intrastrand H-bonds between the polyamino acidic α-helix in the gas phase (blue lines) and adsorbed on the TiO$_2$ surface (red lines).

Optimized Fractionary Coordinates

Optimized fractionary coordinates have been written in the MOLDRAW format (MOLDRAW is freely available at http://www.moldraw.unito.it). Each coordinates block starts with a TITLE record and finishes with a "-1 0 0 0" record. Both input and output files are available in the poly_aa_structure.zip archive.