**Supplementary Information**

# Physicochemical Insights into the Interaction of Cationic Peptides (KR12 and TAT47-57) with Decavanadate: An Integrated ITC and Molecular Dynamics Study

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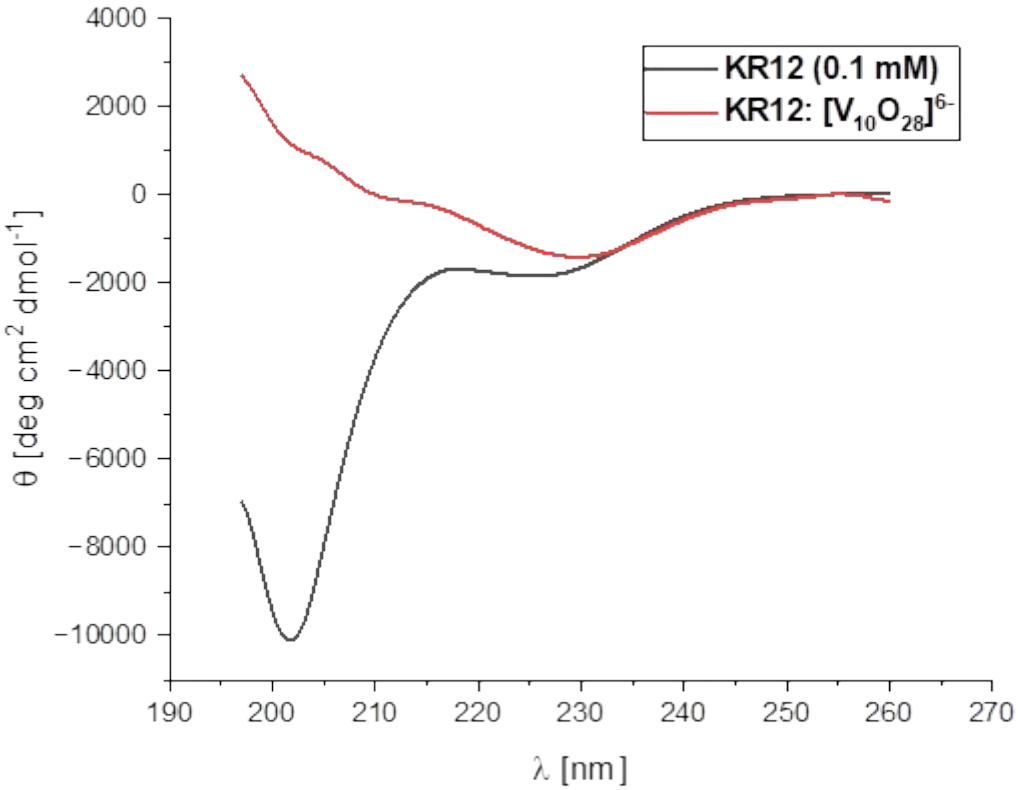



**Fig. S1.** CD spectra of KR12 peptide in the presence of the decavanadate ion $[V_{10}O_{28}]^{6-}$ recorded in the 50 mM sodium cacodylate buffer at pH 5 and 298.15 K.

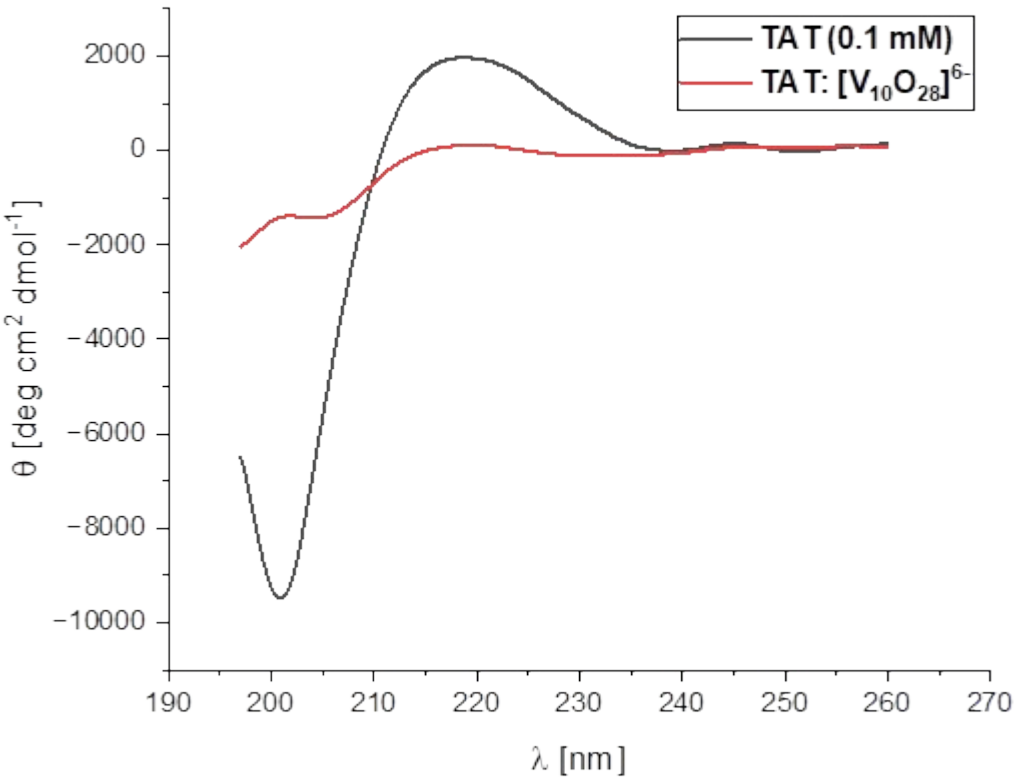



**Fig. S2**. CD spectra of $TAT_{(47-57)}$ peptide in the presence of the decavanadate ion $[V_{10}O_{28}]^{6-}$ recorded in the 50 mM sodium cacodylate buffer at pH 5 and 298.15 K.

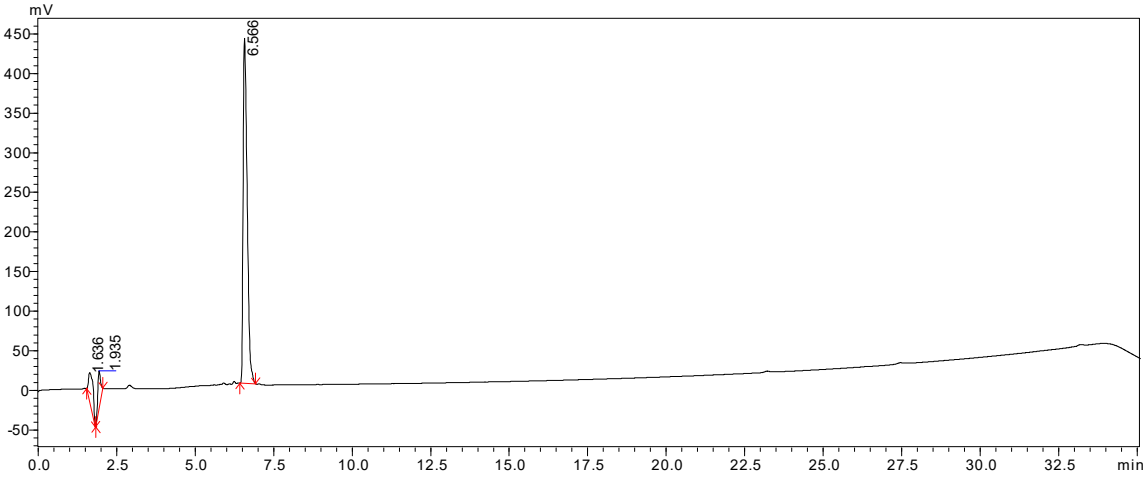



**Fig. S3.** HPLC chromatogram of the pure $TAT_{(47-57)}$.

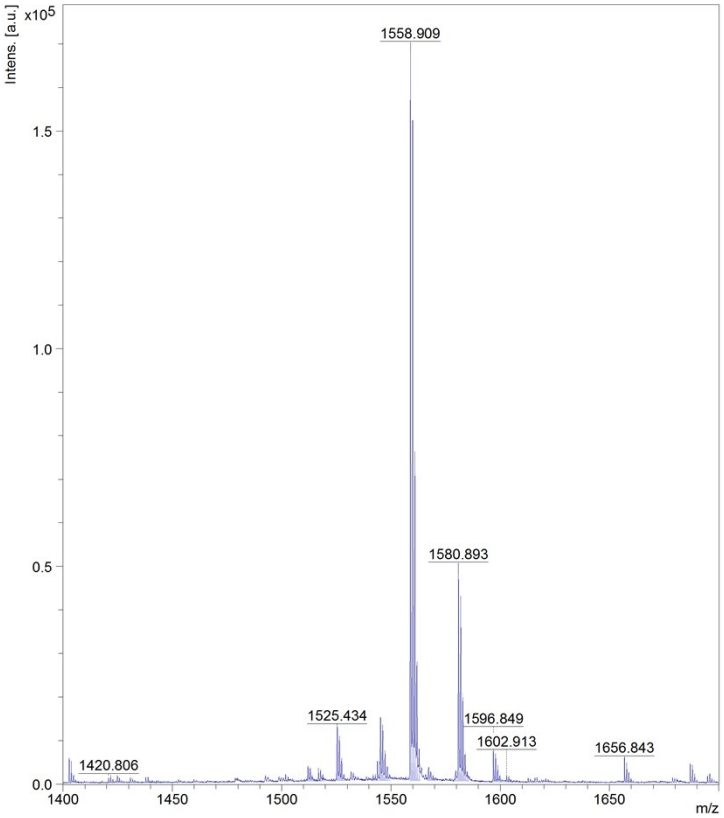
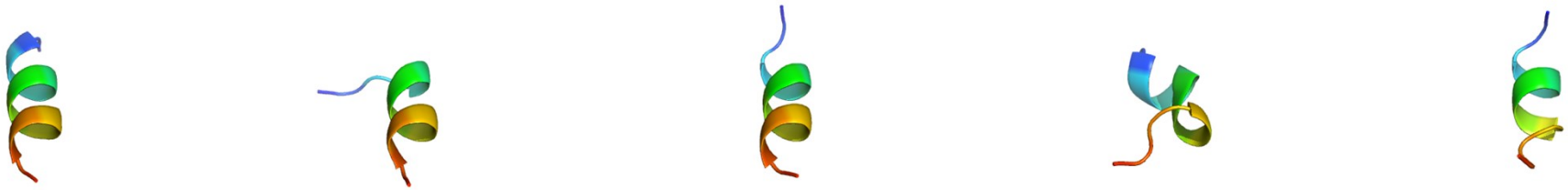



**Fig. S4.** Mass analysis of the pure $TAT_{(47-57)}$. The calculated monoisotopic mass $[M+H]^+$ is 1558.97. The found mass $[M+H]^+$ 1558.91. The second found mass 1580.89 represents an adduct $[M+Na]^+$.

**UNRES analysis**

**KR12 peptide**



40.3% 30.8% 18.9% 6.5% 3.5%

**Fig. S5.** Representative structures of the most populated conformational clusters obtained from UNRES simulations for the **KR12** peptide. The percentage values indicate the probability of each conformational cluster.

**$TAT_{(47-57)}$ peptide**

40.2% 23.6% 15.8% 10.5% 9.9%

**Fig. S6.** Representative structures of the most populated conformational clusters obtained from UNRES simulations for the **$TAT_{(47-57)}$** peptide. The percentage values indicate the probability of each conformational cluster.

**DSSP (*Dictionary of Secondary Structure in Proteins*) analysis**

**KR12 peptide**

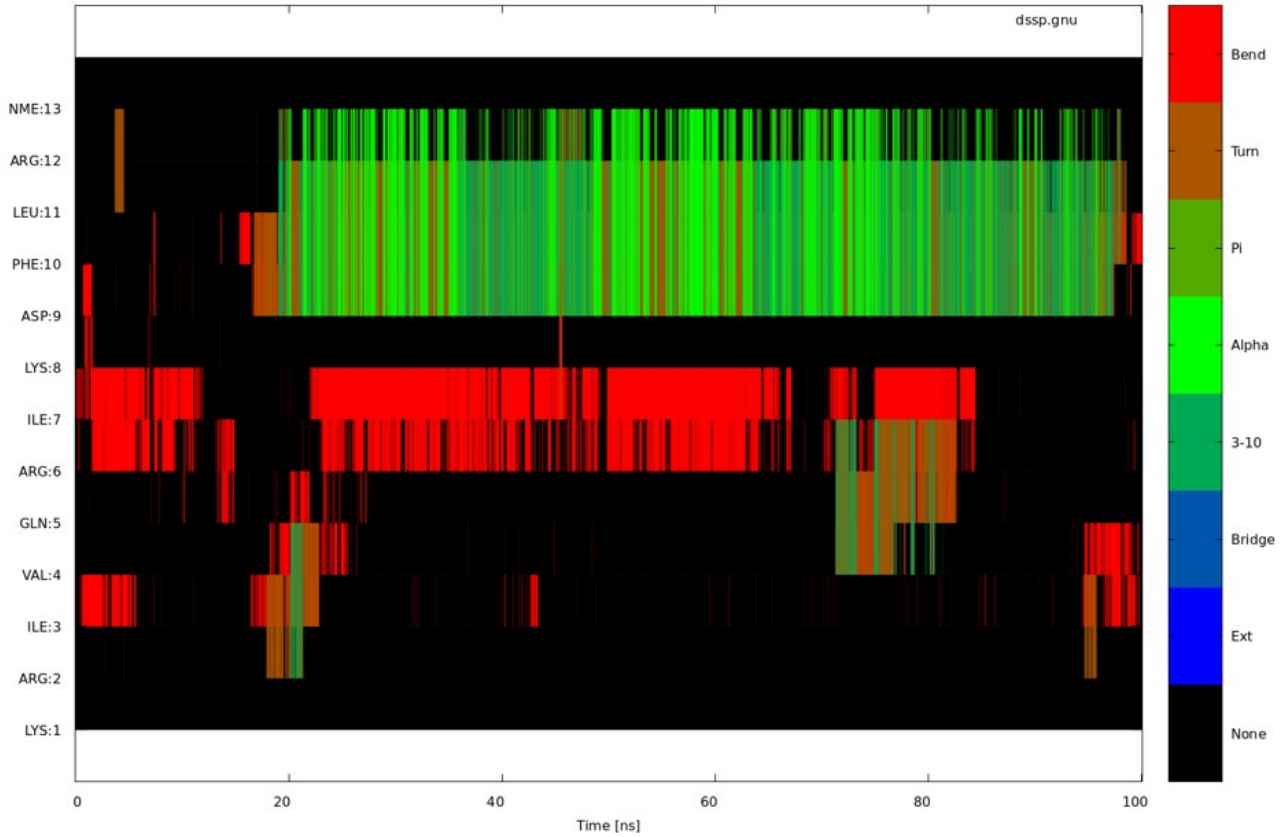



**Fig. S7.** Time evolution of secondary structure elements of the **KR12** peptide obtained from the DSSP analysis for the MD simulation.

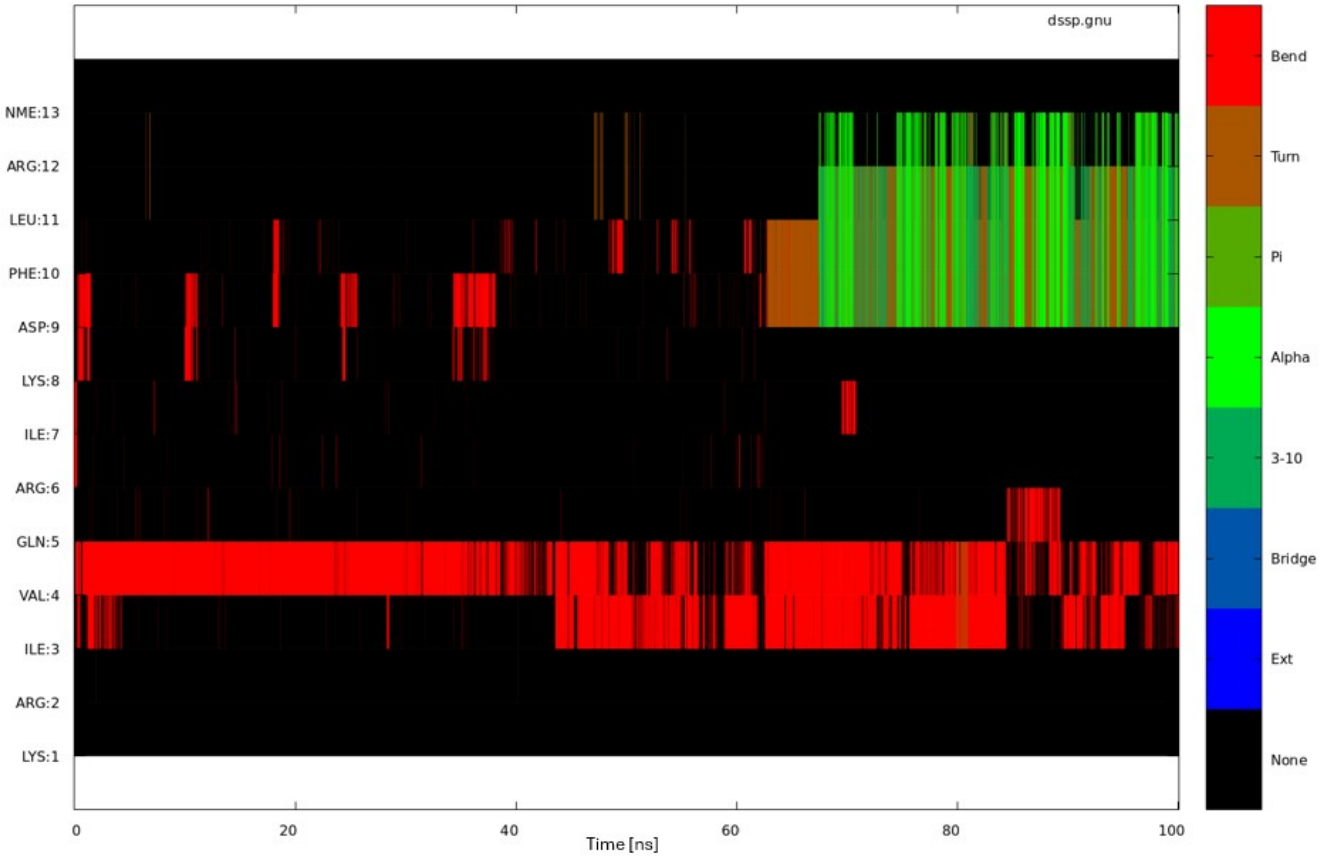



**Fig. S8.** Time evolution of secondary structure elements of the **KR12** peptide in the presence of **decavanadate(V)** ions obtained from the DSSP analysis for the MD simulation.

**DSSP (*Dictionary of Secondary Structure in Proteins*) analysis**

**$TAT_{(47-57)}$ peptide**

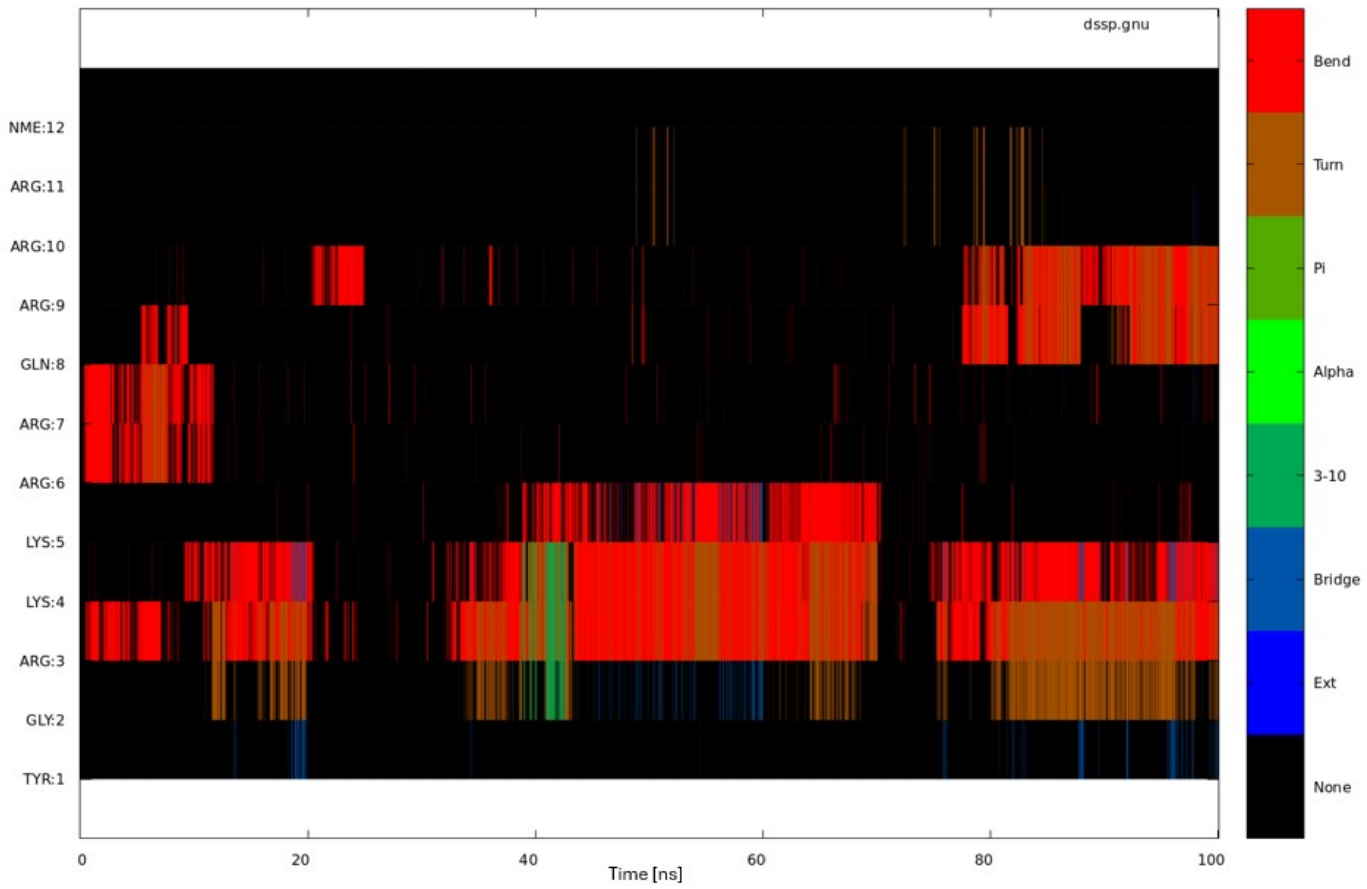



**Fig. S9.** Time evolution of secondary structure elements of the **$TAT_{(47-57)}$** peptide obtained from the DSSP analysis for the MD simulation.

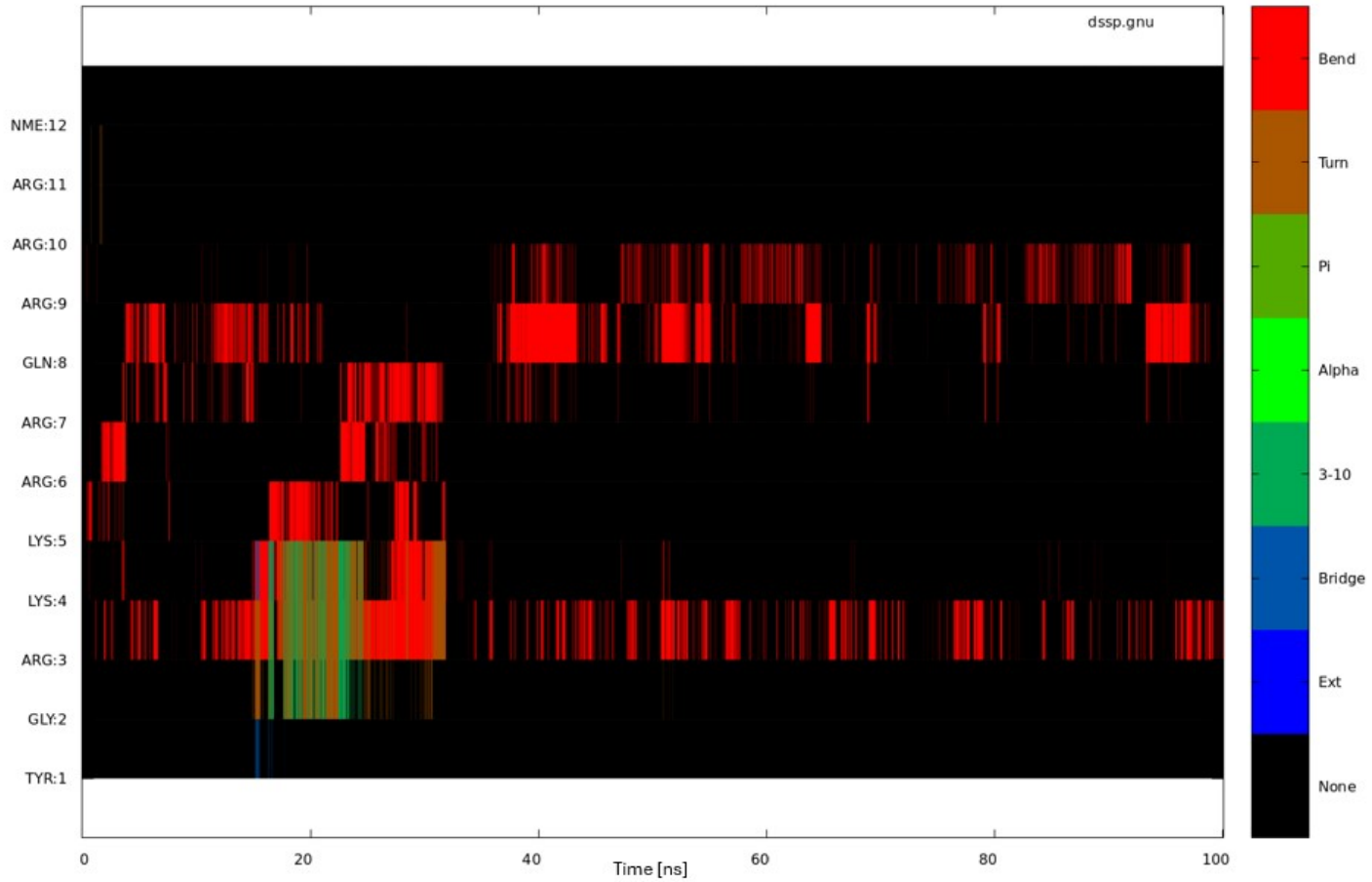



**Fig. S10.** Time evolution of secondary structure elements of the **TAT**$_{(47\text{-}57)}$ peptide in the presence of **decavanadate(V)** ions obtained from the DSSP analysis for the MD simulation.

**Table S1.** Per-residue distances between the KR12 peptide and the center of mass of $[V_{10}O_{28}]^{6-}$

| *Residue* | *Distance, Å* |
|---|---|
| Lys1 | 13.1 ± 3.3 |
| Arg2 | 9.2 ± 1.0 |
| Ile3 | 13.9 ± 1.2 |
| Val4 | 11.7 ± 1.5 |
| Gln5 | 9.7 ± 1.4 |
| Arg6 | 8.7 ± 1.8 |
| Ile7 | 10.8 ± 1.3 |
| Lys8 | 9.8 ± 2.1 |
| Asp9 | 13.0 ± 2.1 |
| Phe10 | 15.6 ± 2.3 |
| Leu11 | 14.7 ± 1.7 |
| Arg12 | 14.8 ± 1.8 |
| NME13 | 18.3 ± 1.8 |

**Table S2.** Per-residue distances between the $TAT_{(47–57)}$ peptide and the center of mass of $[V_{10}O_{28}]^{6-}$.

| *Residue* | *Distance, Å* |
|---|---|
| Tyr1 | 17.0 ± 2.5 |
| Gly2 | 14.4 ± 1.1 |
| Arg3 | 10.1 ± 0.6 |
| Lys4 | 13.1 ± 0.5 |
| Lys5 | 7.9 ± 0.4 |
| Arg6 | 8.2 ± 0.6 |
| Arg7 | 10.8 ± 1.5 |
| Gln8 | 9.6 ± 0.7 |
| Arg9 | 12.7 ± 1.9 |
| Arg10 | 8.5 ± 2.0 |
| Arg11 | 10.1 ± 3.0 |
| NME12 | 12.5 ± 2.3 |

**Table S3.** Per-residue LIE free-energy contributions for the KR12-$[V_{10}O_{28}]^{6-}$ complex.

| *Residue* | *ΔG, kcal/mol* |
|---|---|
| Lys1 | -1.1 ± 1.7 |
| Arg2 | -2.0 ± 1.8 |
| Ile3 | -0.1 ± 0.1 |
| Val4 | -0.2 ± 0.3 |
| Gln5 | -1.4 ± 1.2 |
| Arg6 | -3.8 ± 2.3 |
| Ile7 | -0.7 ± 0.5 |
| Lys8 | -2.4 ± 1.8 |
| Asp9 | 0.1 ± 0.1 |
| Phe10 | -0.1 ± 0.1 |
| Leu11 | -0.1 ± 0.10 |
| Arg12 | -0.2 ± 0.2 |
| NME13 | 0.0± 0.0 |

**Table S4.** Per-residue LIE free-energy contributions for the $TAT_{(47–57)}$-$[V_{10}O_{28}]^{6-}$ complex.

| *Residue* | *ΔG, kcal/mol* |
|---|---|
| Tyr1 | -0.0 ± 0.2 |
| Gly2 | -0.1 ± 0.0 |
| Arg3 | -1.4 ± 1.8 |
| Lys4 | -0.2 ± 0.1 |
| Lys5 | -3.0 ± 1.7 |
| Arg6 | -4.1 ± 1.8 |
| Arg7 | -1.0 ± 0.5 |
| Gln8 | -1.1 ± 0.8 |
| Arg9 | -0.7 ± 1.0 |
| Arg10 | -3.6 ± 2.3 |
| Arg11 | -1.9 ± 1.8 |
| NME12 | -0.0 ± 0.1 |

**KR12 peptide**

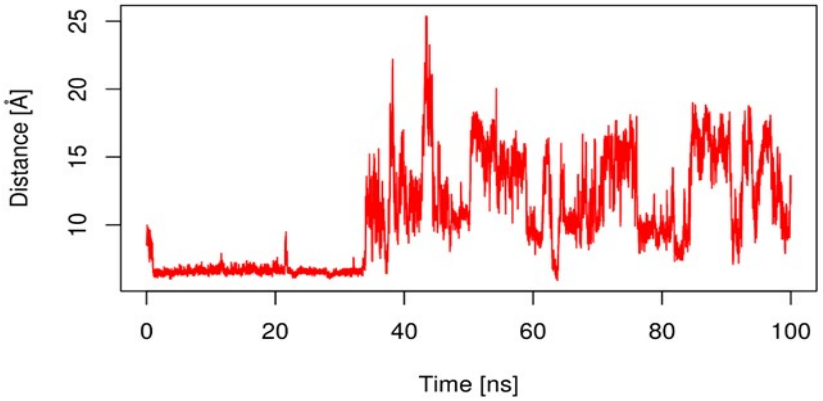



**Fig. S11.** Distance between residue **Lys1** of the **KR12** peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

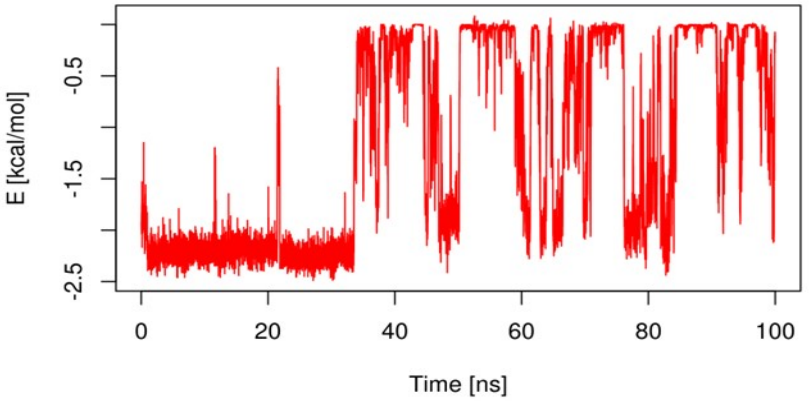



**Fig. S12.** LIE free energy of interaction with the decavanadate for residue **Lys1** of the **KR12** peptide over the entire molecular dynamics trajectory (kcal/mol).

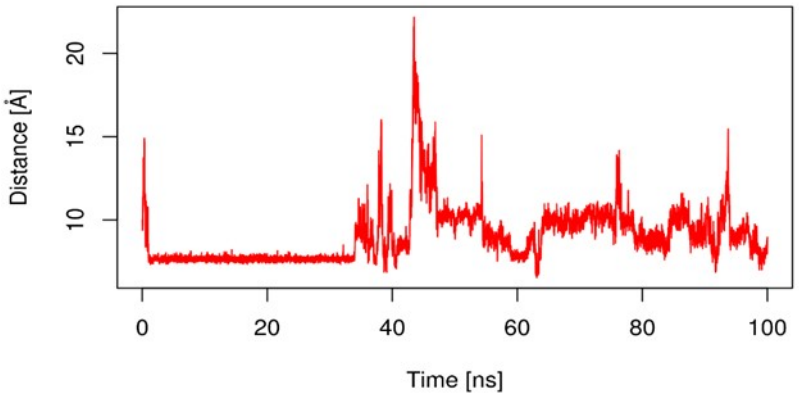



**Fig. S13.** Distance between residue **Arg2** of the **KR12** peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

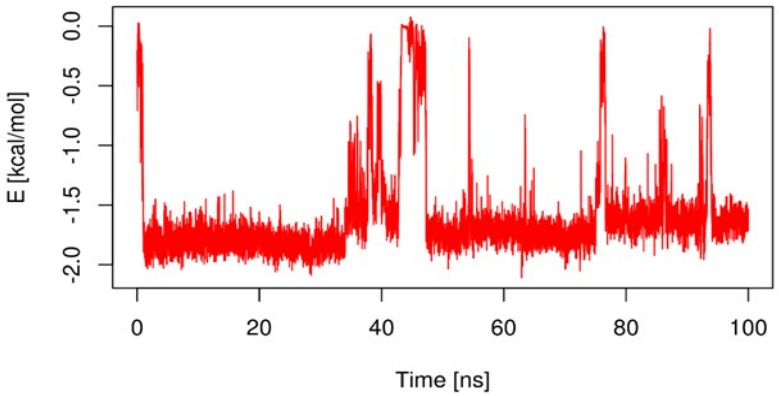



**Fig. S14.** LIE free energy of interaction with the decavanadate for residue **Arg2** of the **KR12** peptide over the entire molecular dynamics trajectory (kcal/mol).

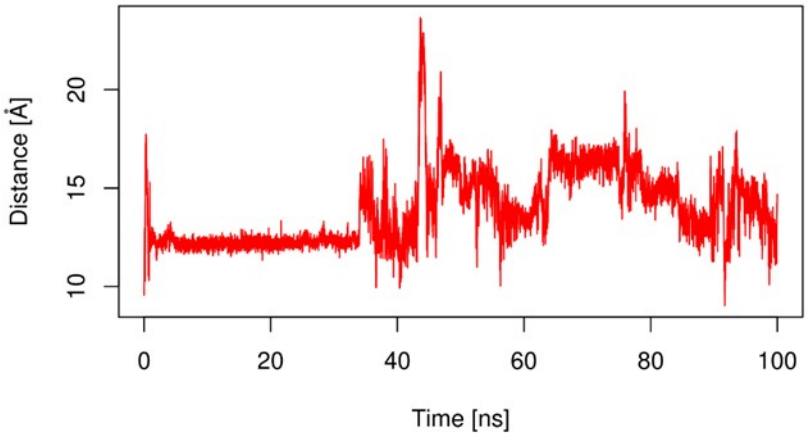



**Fig. S15.** Distance between residue **Ile3** of the **KR12** peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

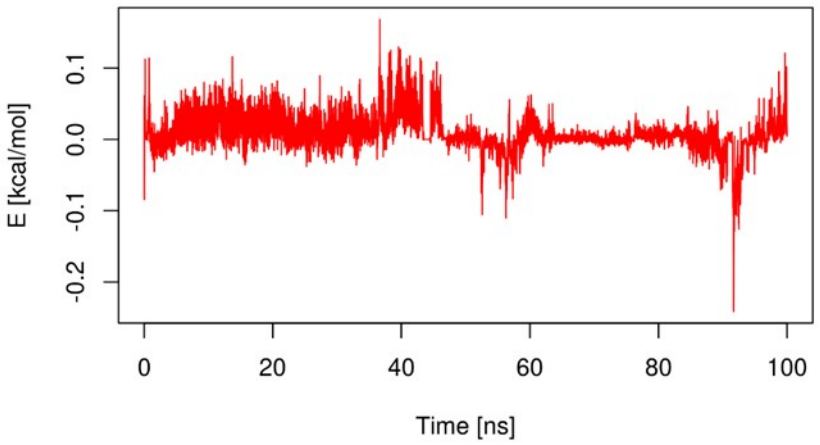



**Fig. S16.** LIE free energy of interaction with the decavanadate for residue **Ile3** of the **KR12** peptide over the entire molecular dynamics trajectory (kcal/mol).

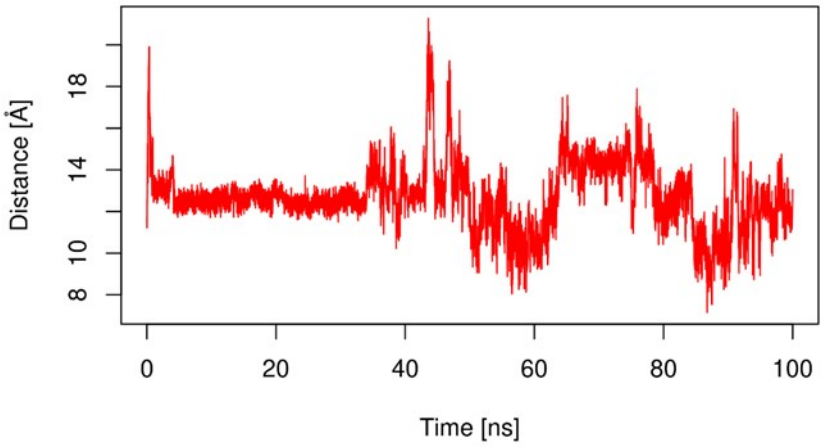



**Fig. S17.** Distance between residue **Val4** of the **KR12** peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

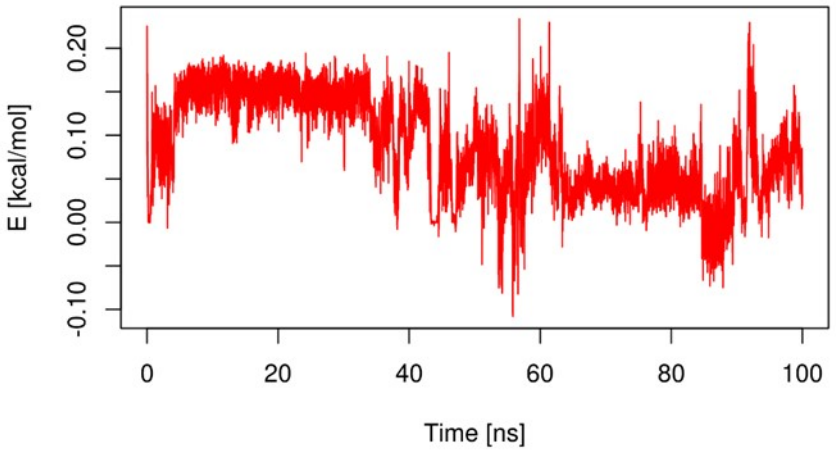



**Fig. S18.** LIE free energy of interaction with the decavanadate for residue **Val4** of the **KR12** peptide over the entire molecular dynamics trajectory (kcal/mol).

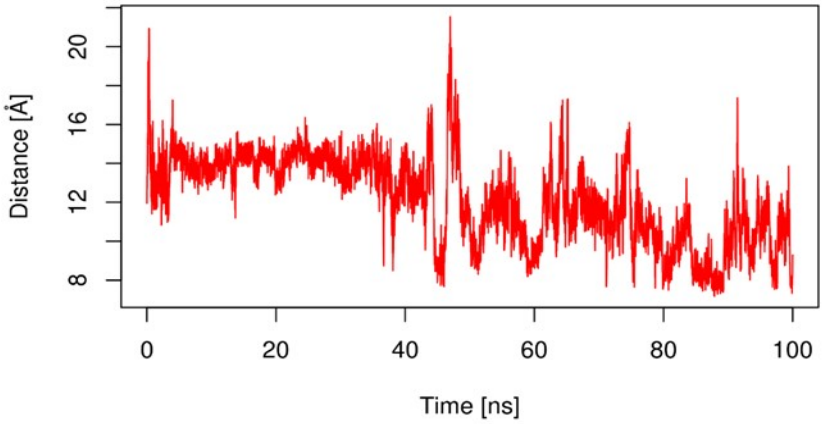



**Fig. S19.** Distance between residue **Gln5** of the **KR12** peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

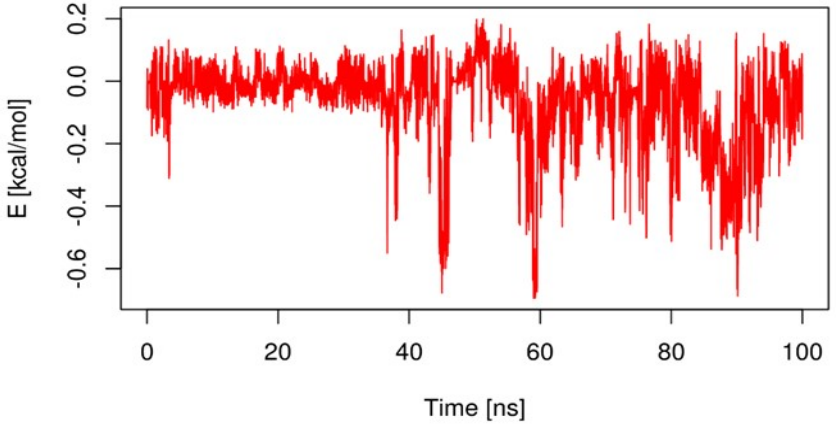



**Fig. S20.** LIE free energy of interaction with the decavanadate for residue **Gln5** of the **KR12** peptide over the entire molecular dynamics trajectory (kcal/mol).

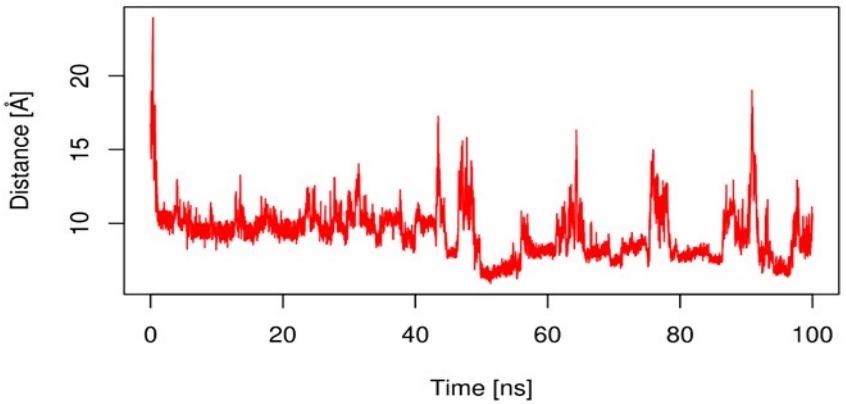



**Fig. S21.** Distance between residue **Arg6** of the **KR12** peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

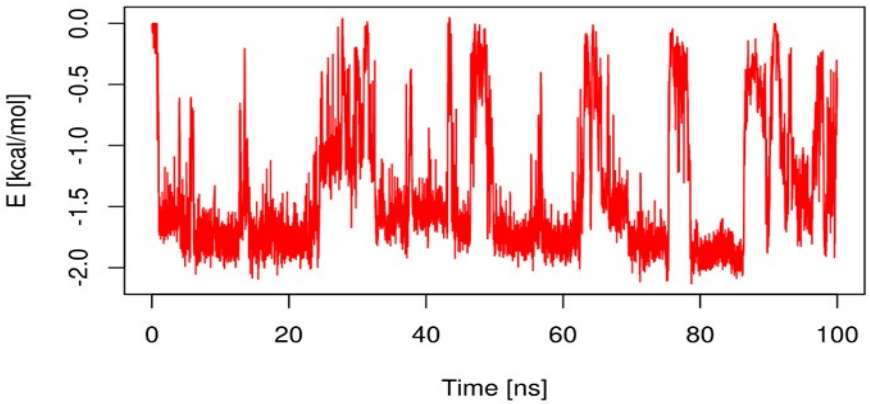



**Fig. S22.** LIE free energy of interaction with the decavanadate for residue **Arg6** of the **KR12** peptide over the entire molecular dynamics trajectory (kcal/mol).

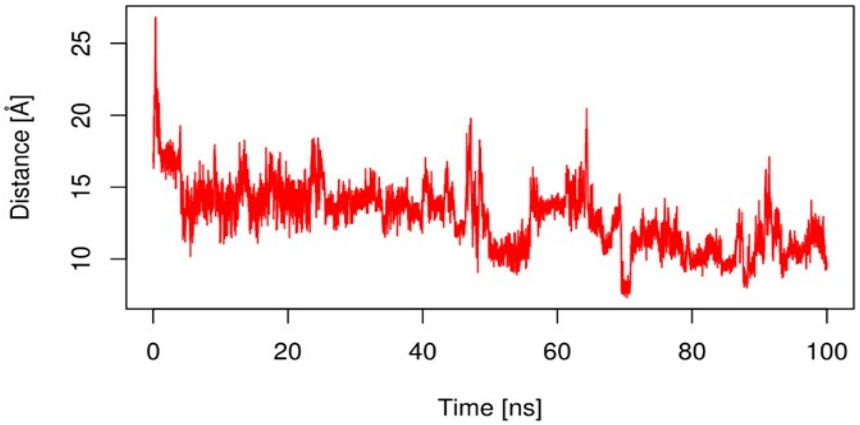



**Fig. S23.** Distance between residue **Ile7** of the **KR12** peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

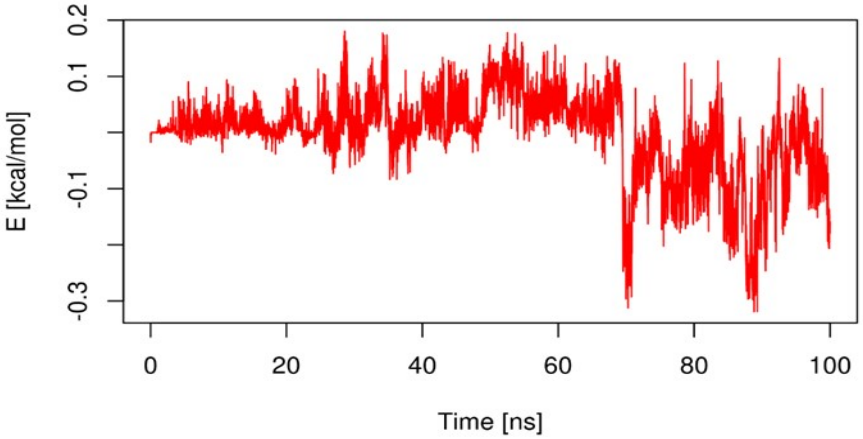



**Fig. S24.** LIE free energy of interaction with the decavanadate for residue **Ile7** of the **KR12** peptide over the entire molecular dynamics trajectory (kcal/mol).

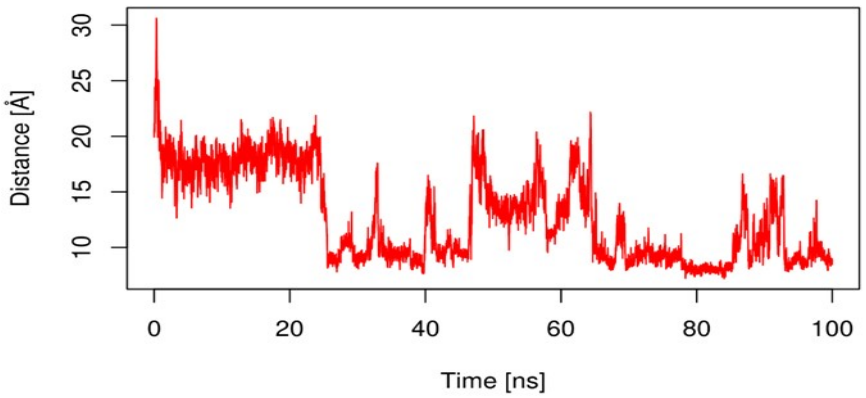



**Fig. S25.** Distance between residue **Lys8** of the **KR12** peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

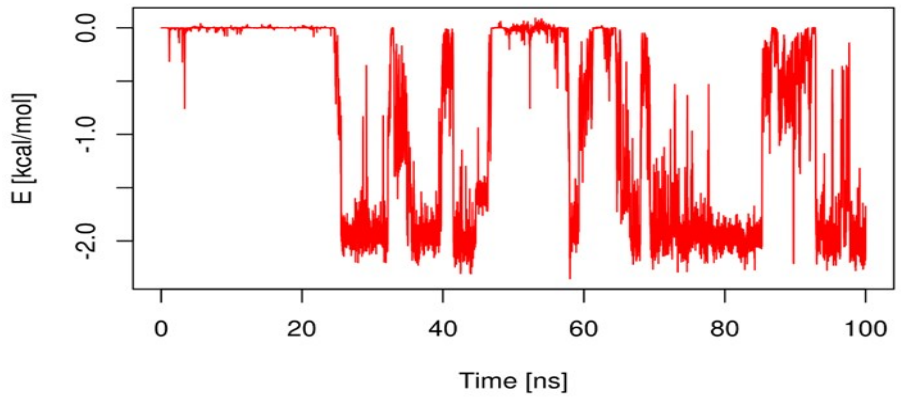



**Fig. S26.** LIE free energy of interaction with the decavanadate for residue **Lys8** of the **KR12** peptide over the entire molecular dynamics trajectory (kcal/mol).

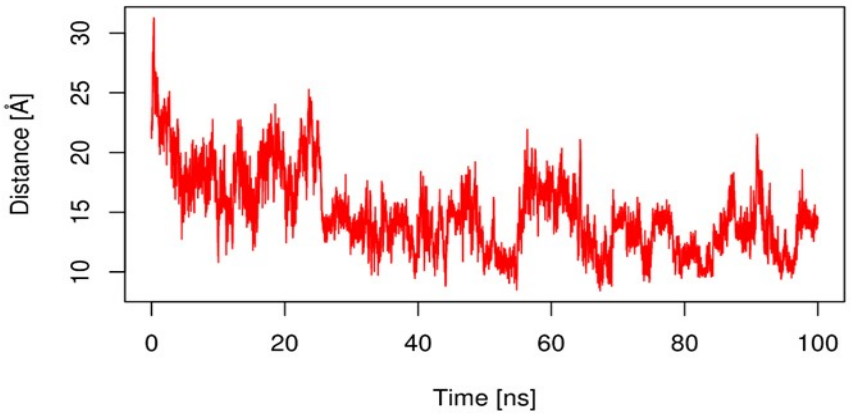



**Fig. S27.** Distance between residue **Asp9** of the **KR12** peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

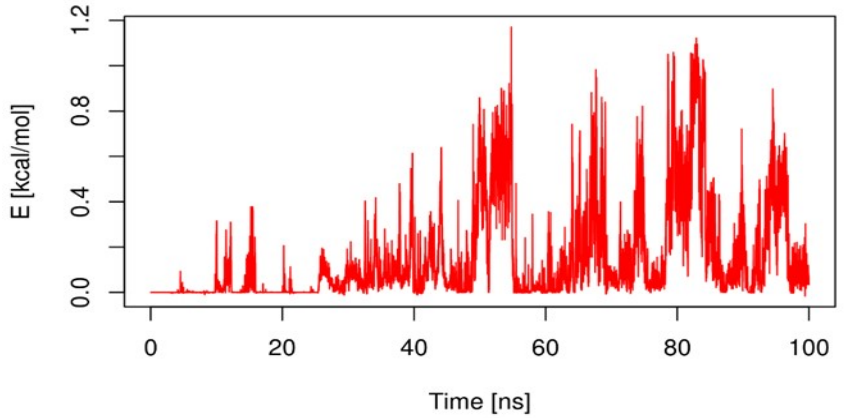



**Fig. S28.** LIE free energy of interaction with the decavanadate for residue **Asp9** of the **KR12** peptide over the entire molecular dynamics trajectory (kcal/mol).

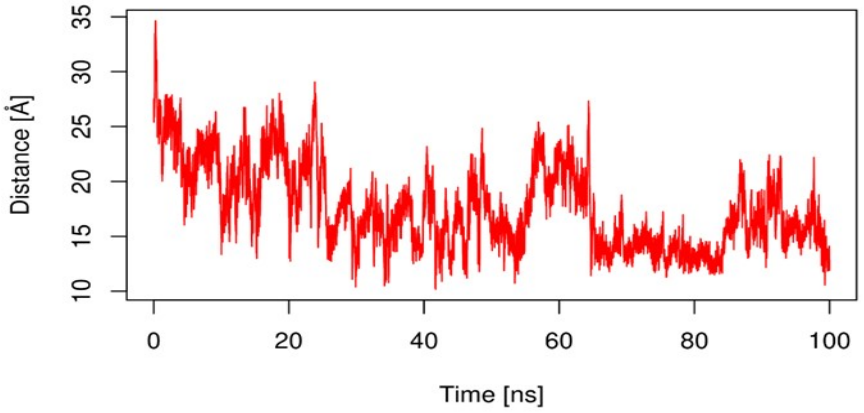



**Fig. S29.** Distance between residue **Phe10** of the **KR12** peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

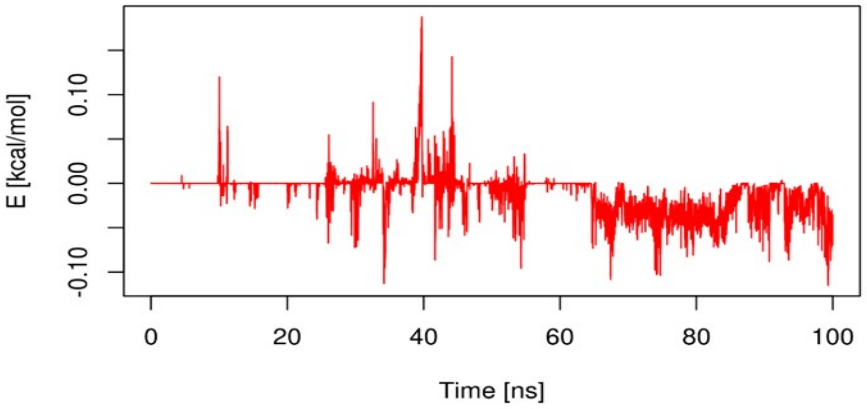



**Fig. S30.** LIE free energy of interaction with the decavanadate for residue **Phe10** of the **KR12** peptide over the entire molecular dynamics trajectory (kcal/mol).

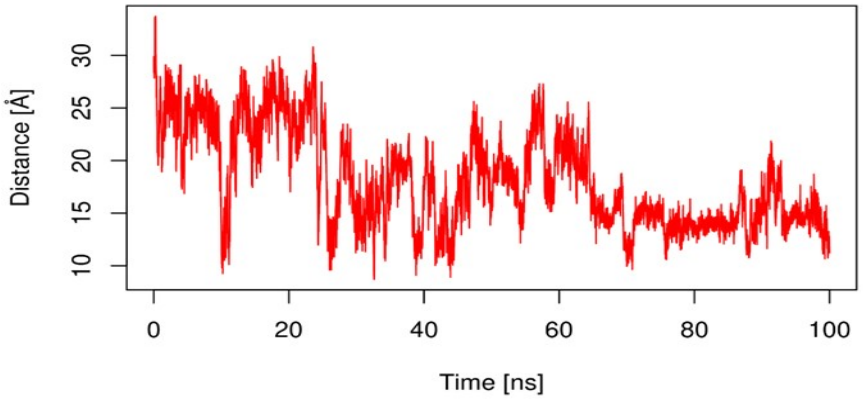



**Fig. S31.** Distance between residue **Leu11** of the **KR12** peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

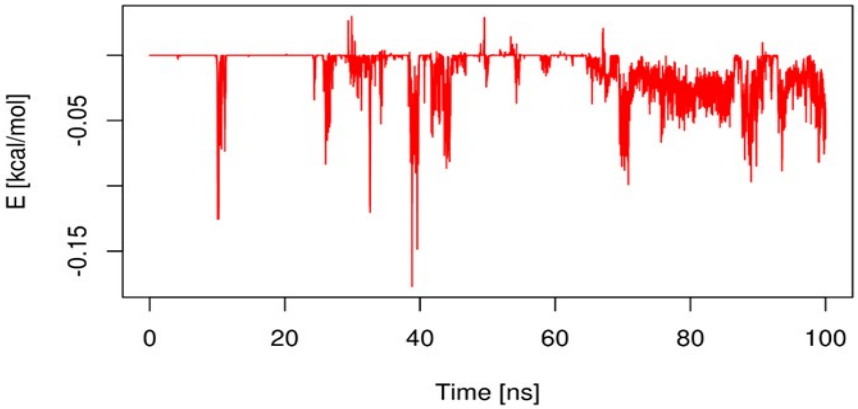



**Fig. S32.** LIE free energy of interaction with the decavanadate for residue **Leu11** of the **KR12** peptide over the entire molecular dynamics trajectory (kcal/mol).

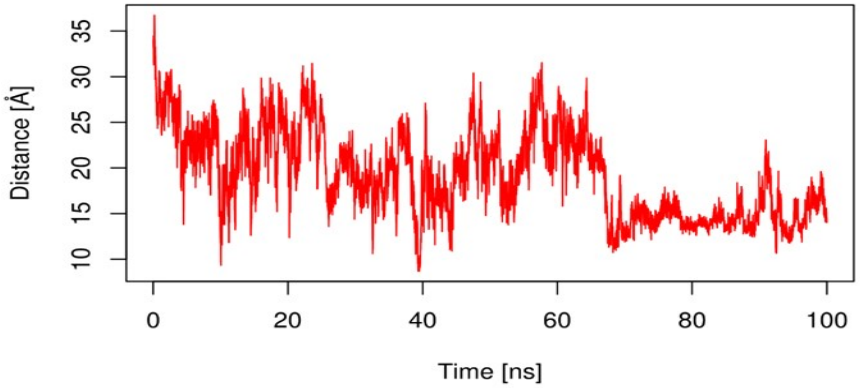



**Fig. S33.** Distance between residue **Arg12** of the **KR12** peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

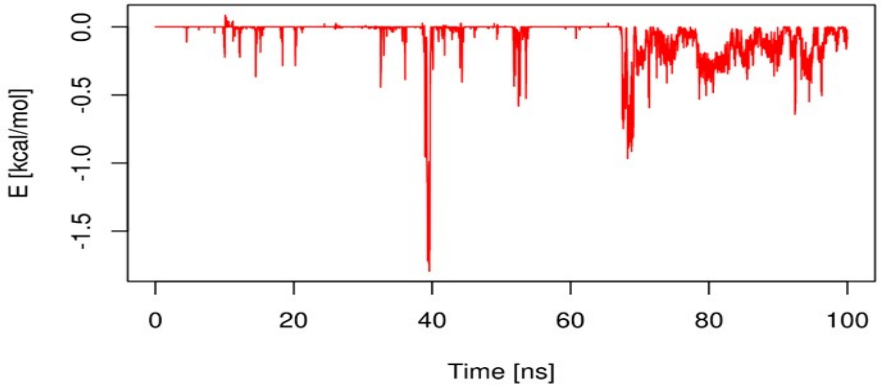



**Fig. S34.** LIE free energy of interaction with the decavanadate for residue **Arg12** of the **KR12** peptide over the entire molecular dynamics trajectory (kcal/mol).

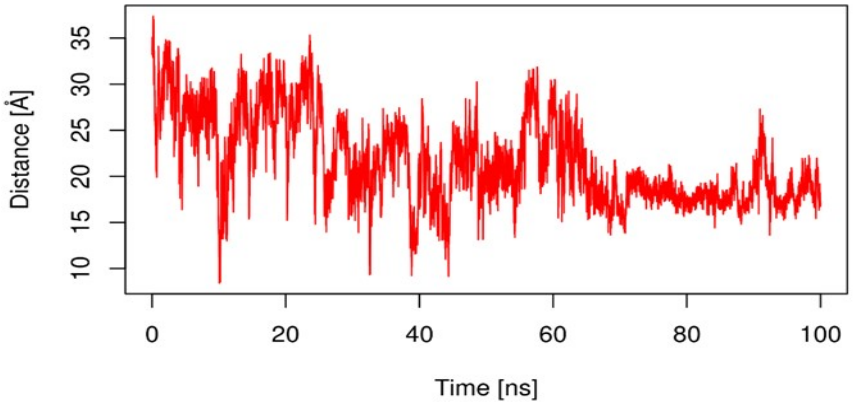



**Fig. S35.** Distance between residue **NME13** of the **KR12** peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

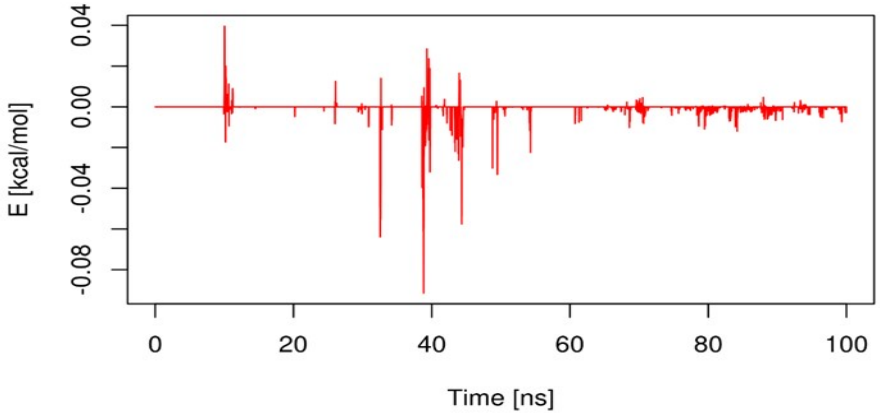



**Fig. S36.** LIE free energy of interaction with the decavanadate for residue **NME13** of the **KR12** peptide over the entire molecular dynamics trajectory (kcal/mol).

**TAT$_{(47-57)}$ peptide**

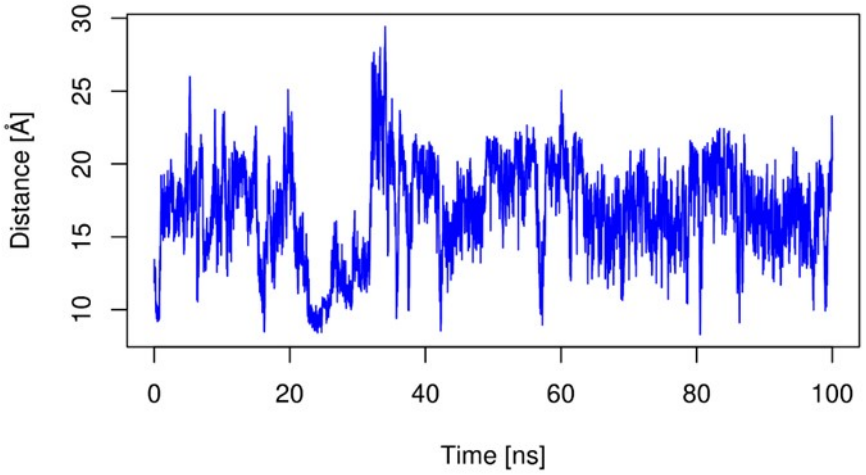



**Fig. S37.** Distance between residue **Tyr1** of the **TAT**$_{(47-57)}$ peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

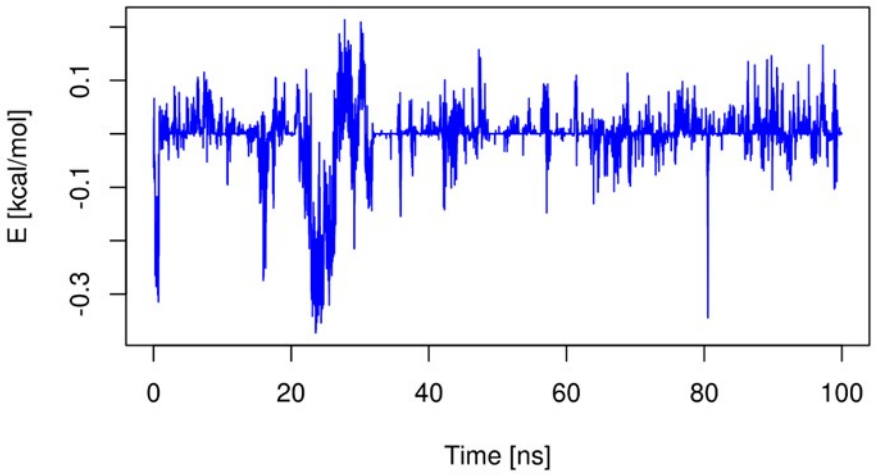



**Fig. S38.** LIE free energy of interaction with the decavanadate for residue **Tyr1** of the **TAT**$_{(47-57)}$ peptide over the entire molecular dynamics trajectory (kcal/mol).

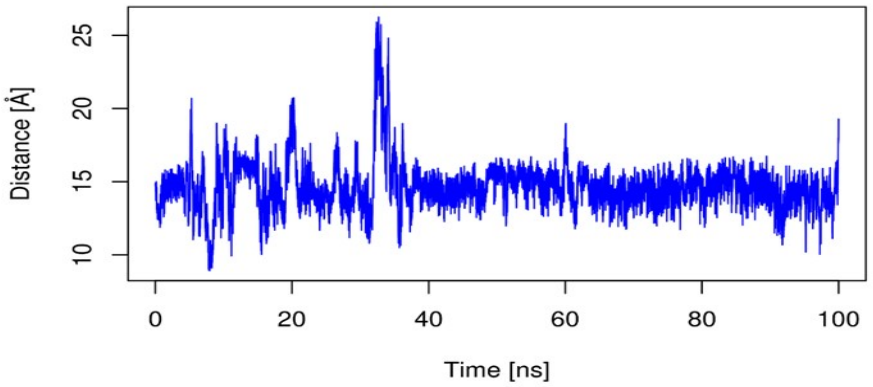



**Fig. S39.** Distance between residue **Gly2** of the **TAT**$_{(47\text{-}57)}$ peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

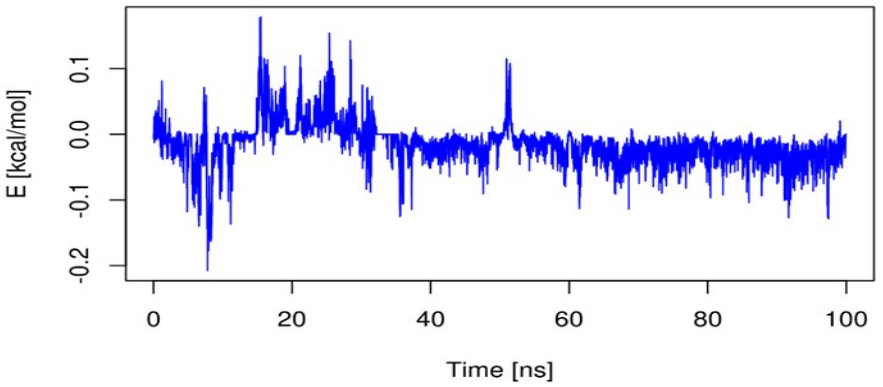



**Fig. S40.** LIE free energy of interaction with the decavanadate for residue **Gly2** of the **TAT**$_{(47\text{-}57)}$ peptide over the entire molecular dynamics trajectory (kcal/mol).

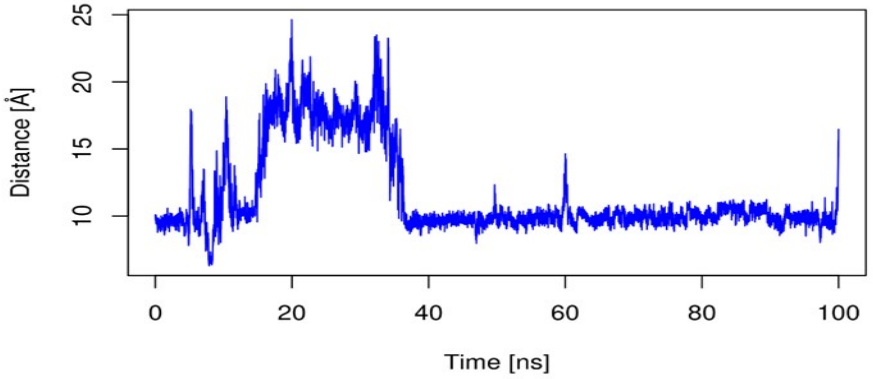



**Fig. S41.** Distance between residue **Arg3** of the **TAT**$_{(47\text{-}57)}$ peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

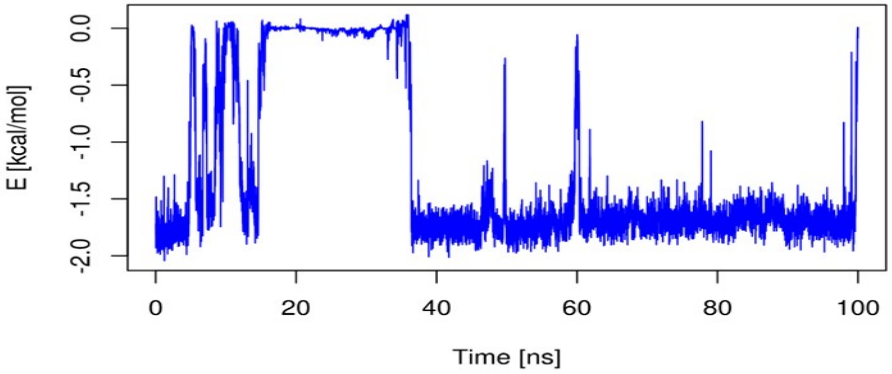



**Fig. S42.** LIE free energy of interaction with the decavanadate for residue **Arg3** of the **TAT**$_{(47\text{-}57)}$ peptide over the entire molecular dynamics trajectory (kcal/mol).

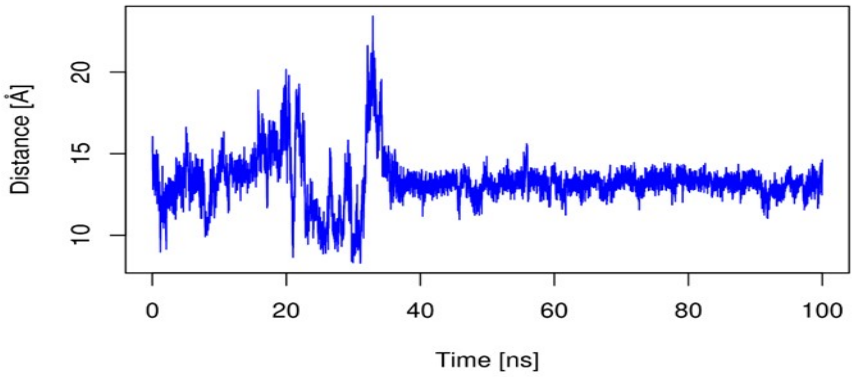



**Fig. S43.** Distance between residue **Lys4** of the **TAT**$_{(47\text{-}57)}$ peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

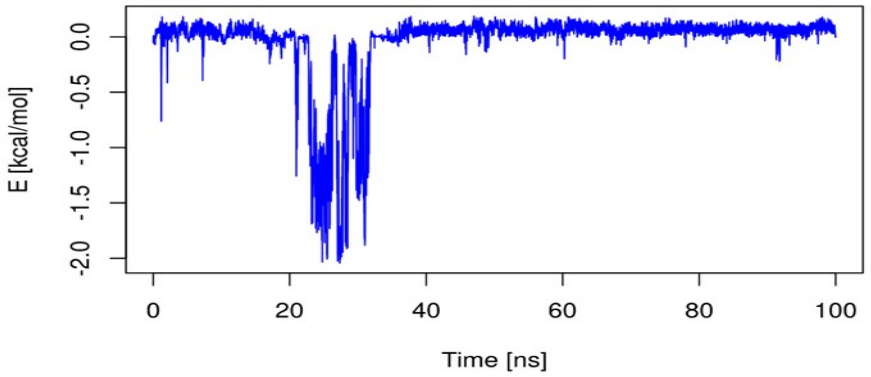



**Fig. S44.** LIE free energy of interaction with the decavanadate for residue **Lys4** of the **TAT**$_{(47\text{-}57)}$ peptide over the entire molecular dynamics trajectory (kcal/mol).

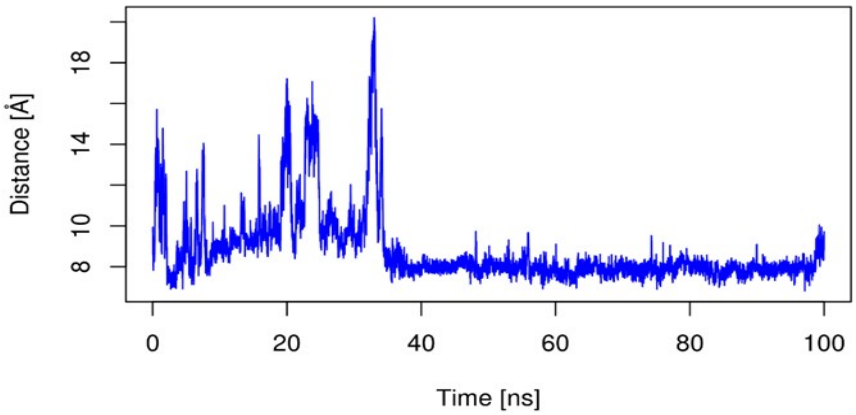



**Fig. S45.** Distance between residue **Lys5** of the **TAT**$_{(47\text{-}57)}$ peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

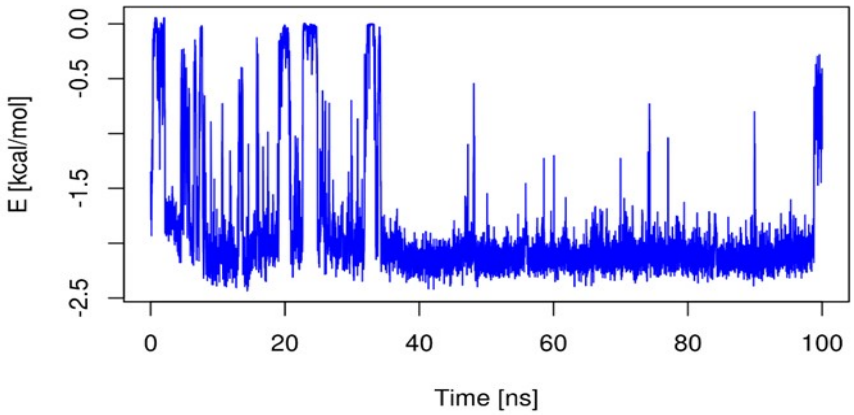



**Fig. S46.** LIE free energy of interaction with the decavanadate for residue **Lys5** of the **TAT**$_{(47\text{-}57)}$ peptide over the entire molecular dynamics trajectory (kcal/mol).

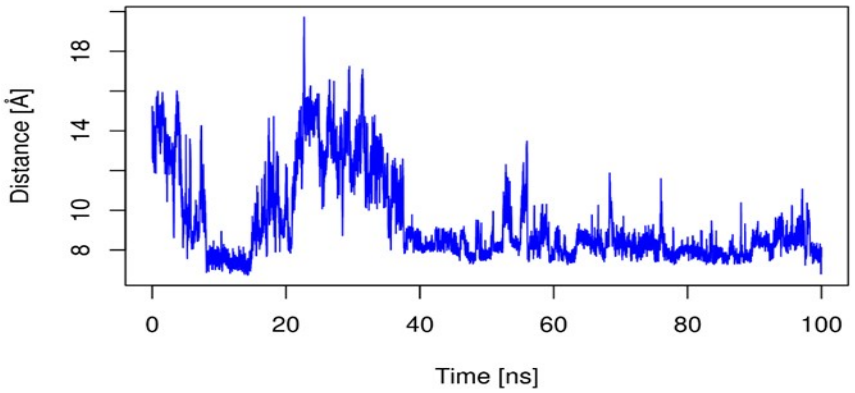



**Fig. S47.** Distance between residue **Arg6** of the **TAT**$_{(47\text{-}57)}$ peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

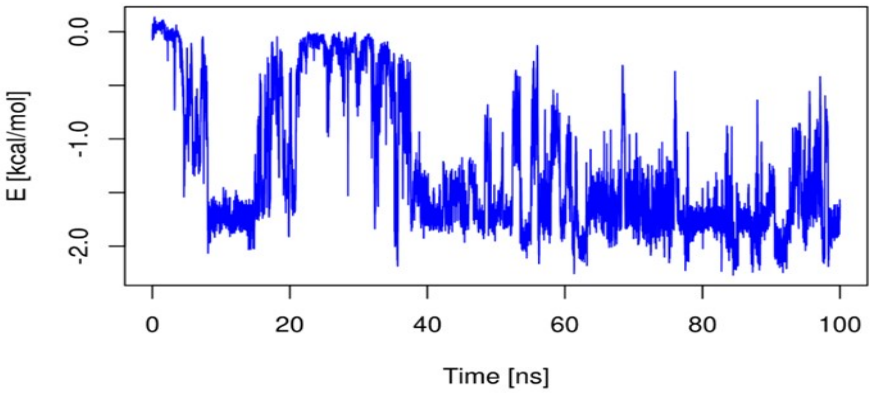



**Fig. S48.** LIE free energy of interaction with the decavanadate for residue **Arg6** of the **TAT**$_{(47\text{-}57)}$ peptide over the entire molecular dynamics trajectory (kcal/mol).

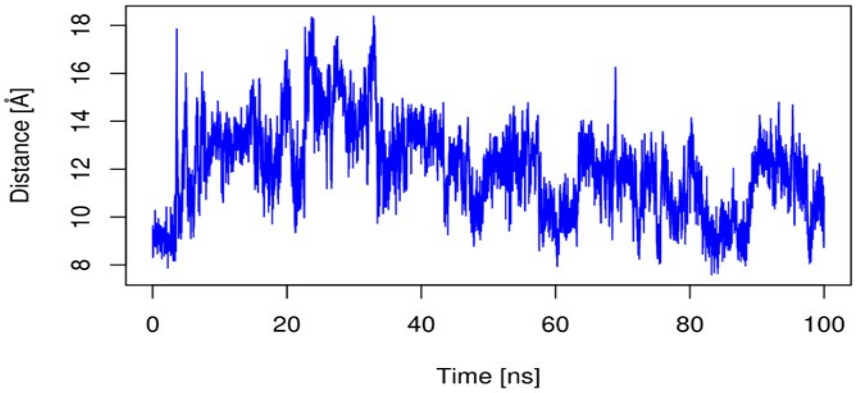



**Fig. S49.** Distance between residue **Arg7** of the **TAT**$_{(47\text{-}57)}$ peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

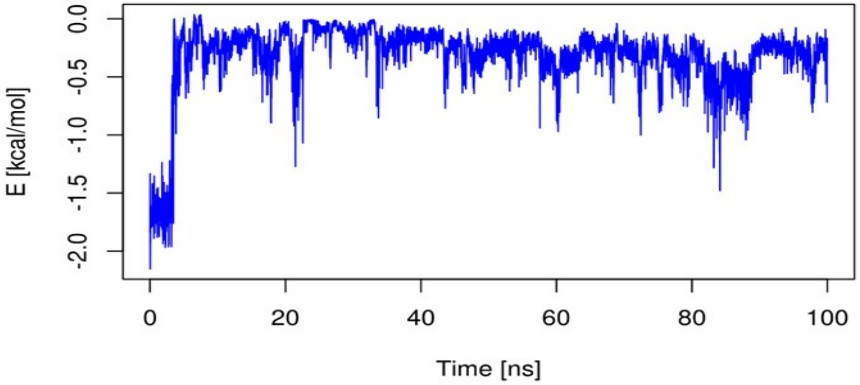



**Fig. S50.** LIE free energy of interaction with the decavanadate for residue **Arg7** of the **TAT**$_{(47\text{-}57)}$ peptide over the entire molecular dynamics trajectory (kcal/mol).

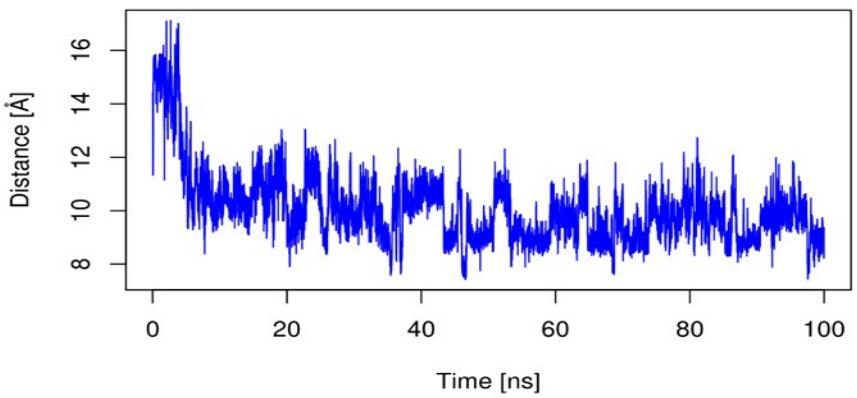



**Fig. S51.** Distance between residue **Gln8** of the **TAT**$_{(47\text{-}57)}$ peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

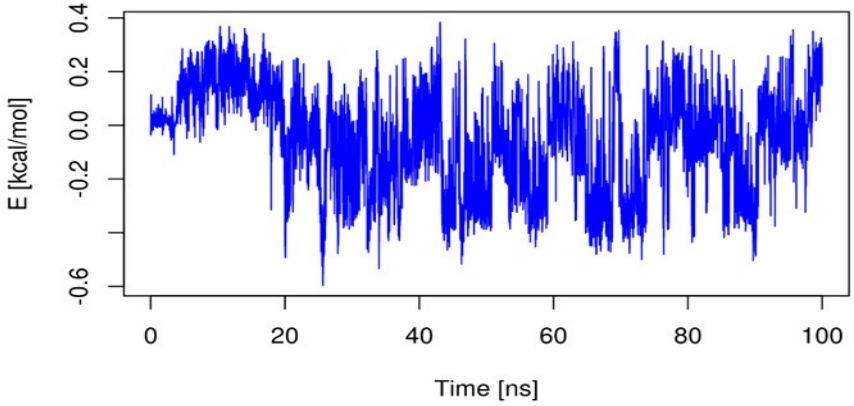



**Fig. S52.** LIE free energy of interaction with the decavanadate for residue **Gln8** of the **TAT**$_{(47\text{-}57)}$ peptide over the entire molecular dynamics trajectory (kcal/mol).

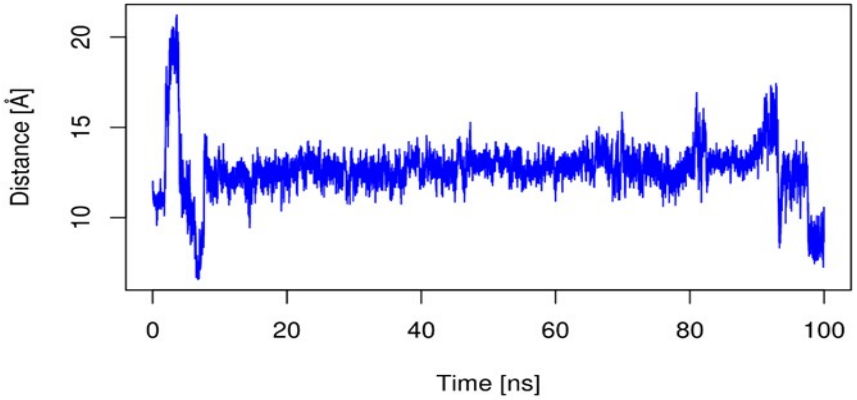



**Fig. S53.** Distance between residue **Arg9** of the **TAT**$_{(47\text{-}57)}$ peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

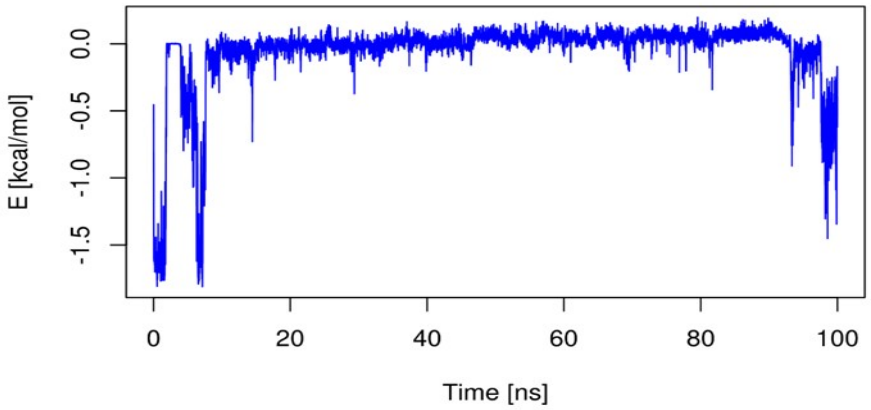



**Fig. S54.** LIE free energy of interaction with the decavanadate for residue **Arg9** of the **TAT**$_{(47\text{-}57)}$ peptide over the entire molecular dynamics trajectory (kcal/mol).

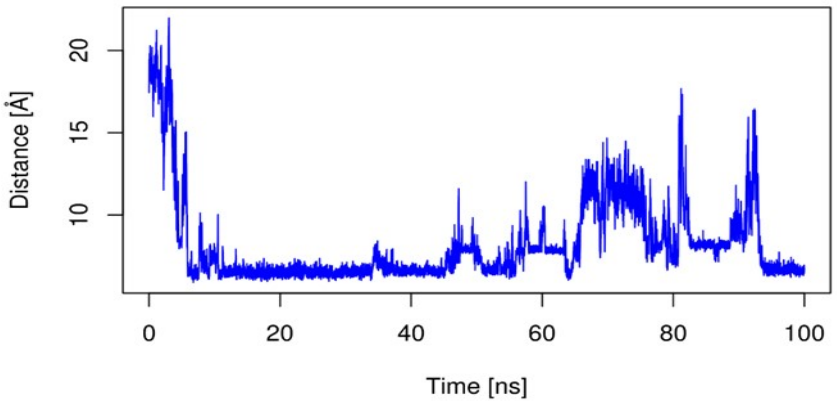



**Fig. S55.** Distance between residue **Arg10** of the **TAT**$_{(47\text{-}57)}$ peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

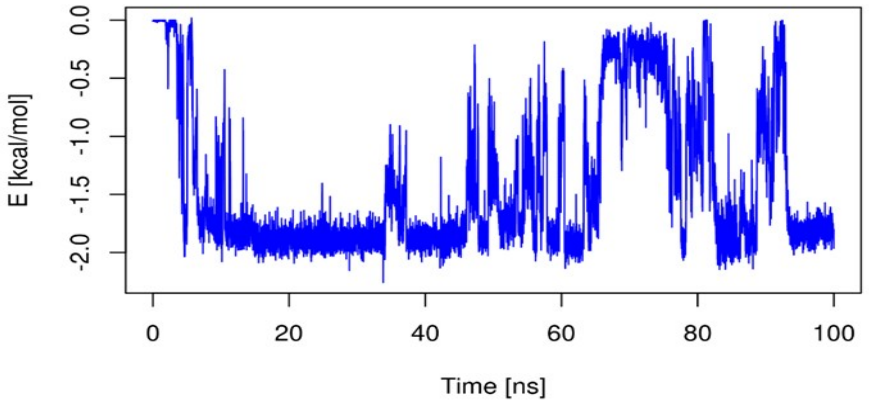



**Fig. S56.** LIE free energy of interaction with the decavanadate for residue **Arg10** of the **TAT**$_{(47\text{-}57)}$ peptide over the entire molecular dynamics trajectory (kcal/mol).

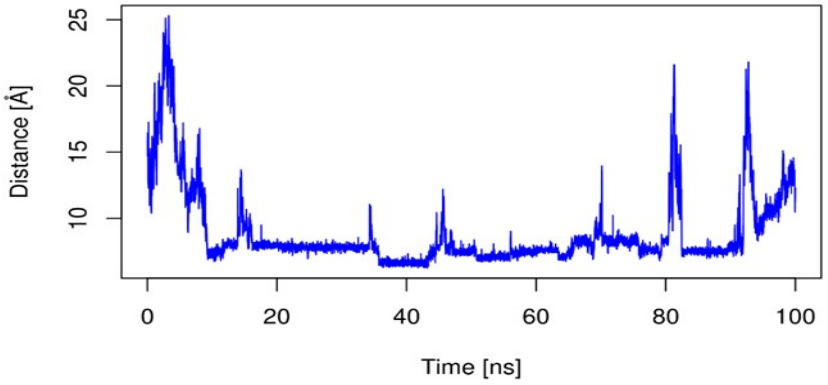



**Fig. S57.** Distance between residue **Arg11** of the **TAT**$_{(47\text{-}57)}$ peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

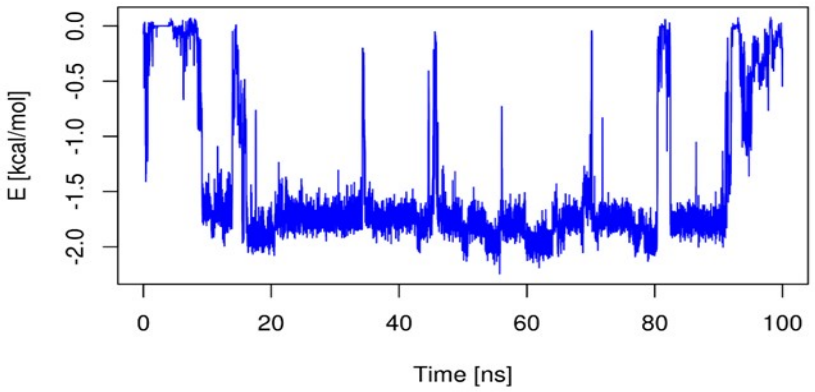



**Fig. S58.** LIE free energy of interaction with the decavanadate for residue **Arg11** of the **TAT**$_{(47\text{-}57)}$ peptide over the entire molecular dynamics trajectory (kcal/mol).

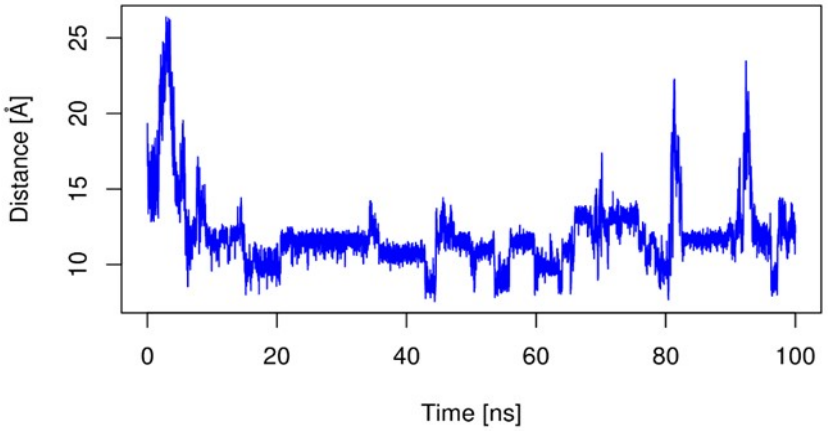



**Fig. S59.** Distance between residue **NME12** of the **TAT**$_{(47\text{-}57)}$ peptide and the center of mass of the decavanadate over the entire molecular dynamics trajectory (Å).

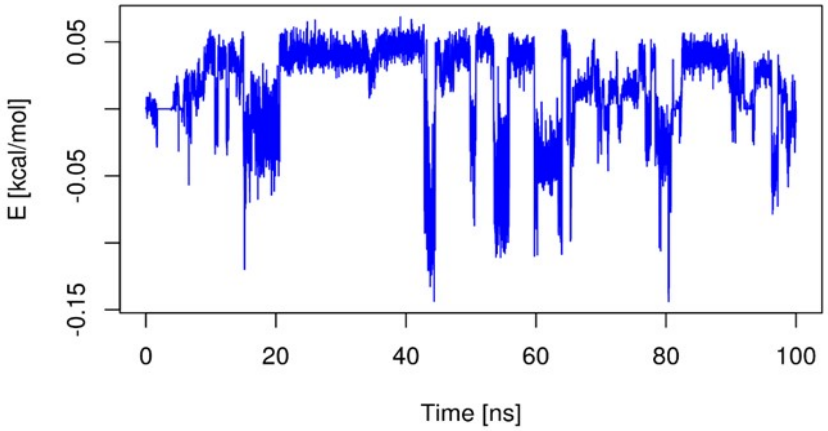



**Fig. S60.** LIE free energy of interaction with the decavanadate for residue **NME12** of the **TAT**$_{(47\text{-}57)}$ peptide over the entire molecular dynamics trajectory (kcal/mol).