

## Supplementary Material

### Predictions of the chiral self-assembling of TPPS<sub>4</sub> porphyrin aggregates perturbed by molecular rotations

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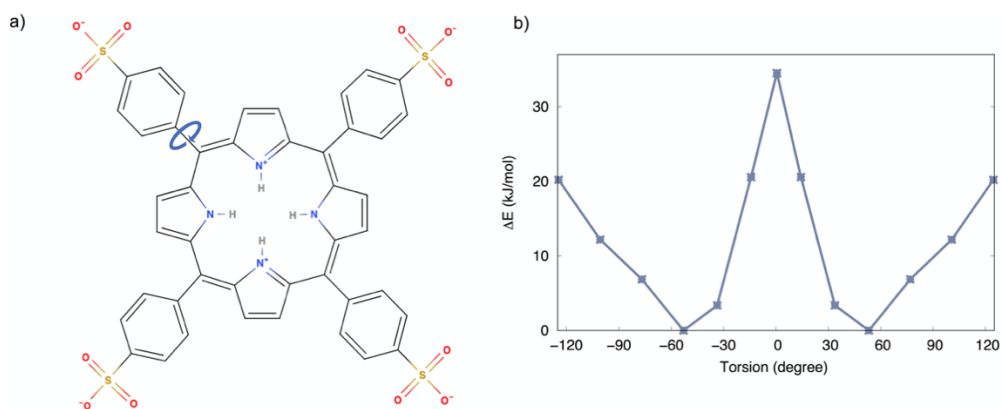
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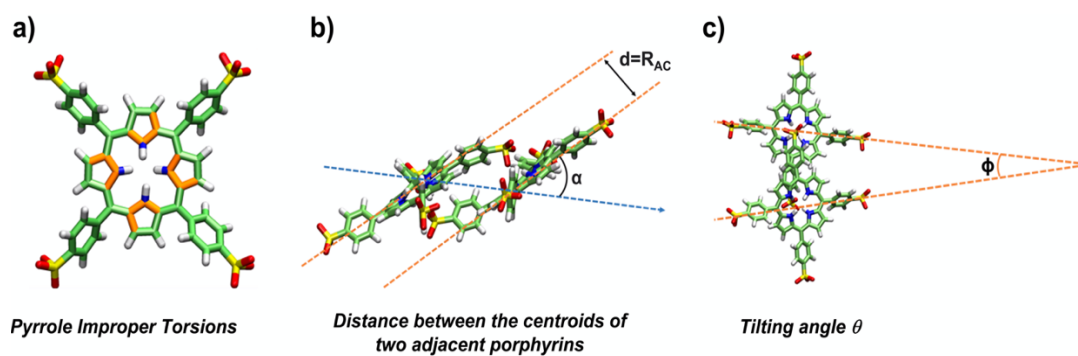
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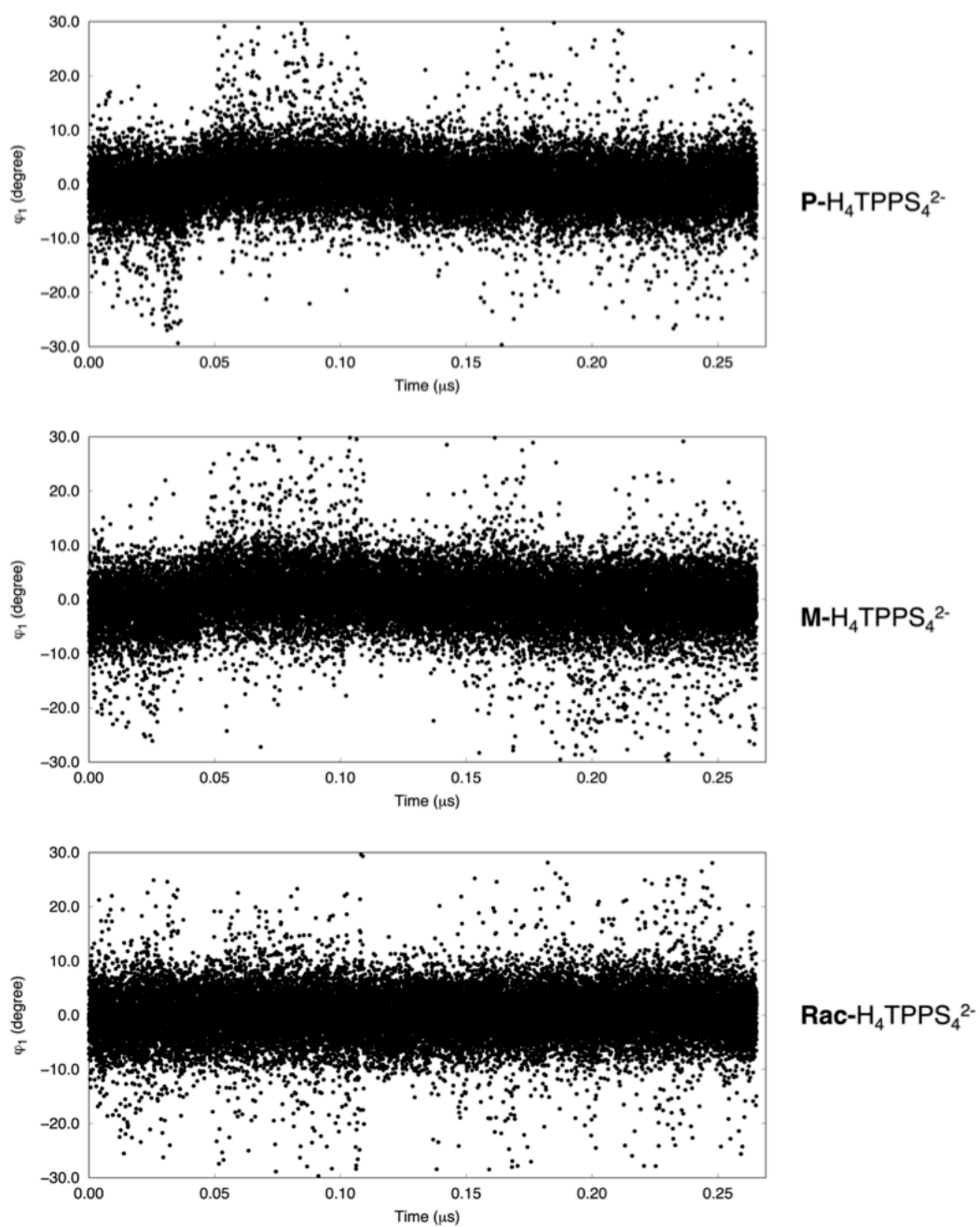
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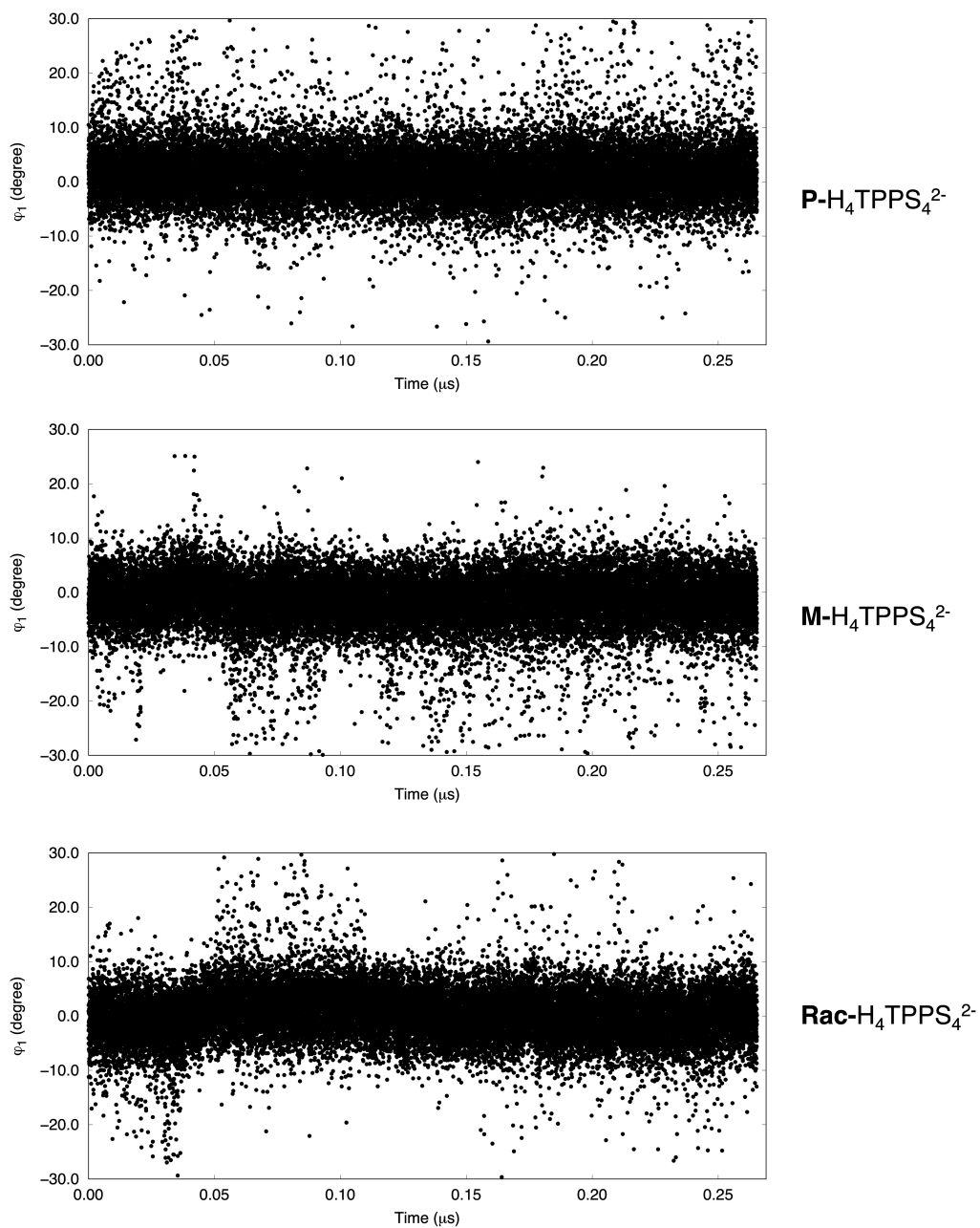
**Figure S1.** a) A sketch of the  $H_4TPPS_4^{2-}$  molecule under study. b) Adiabatic free-energy barriers related to the internal rotation of a single *meso*-sulfonatophenyl group attached to a porphyrin macrocycle.



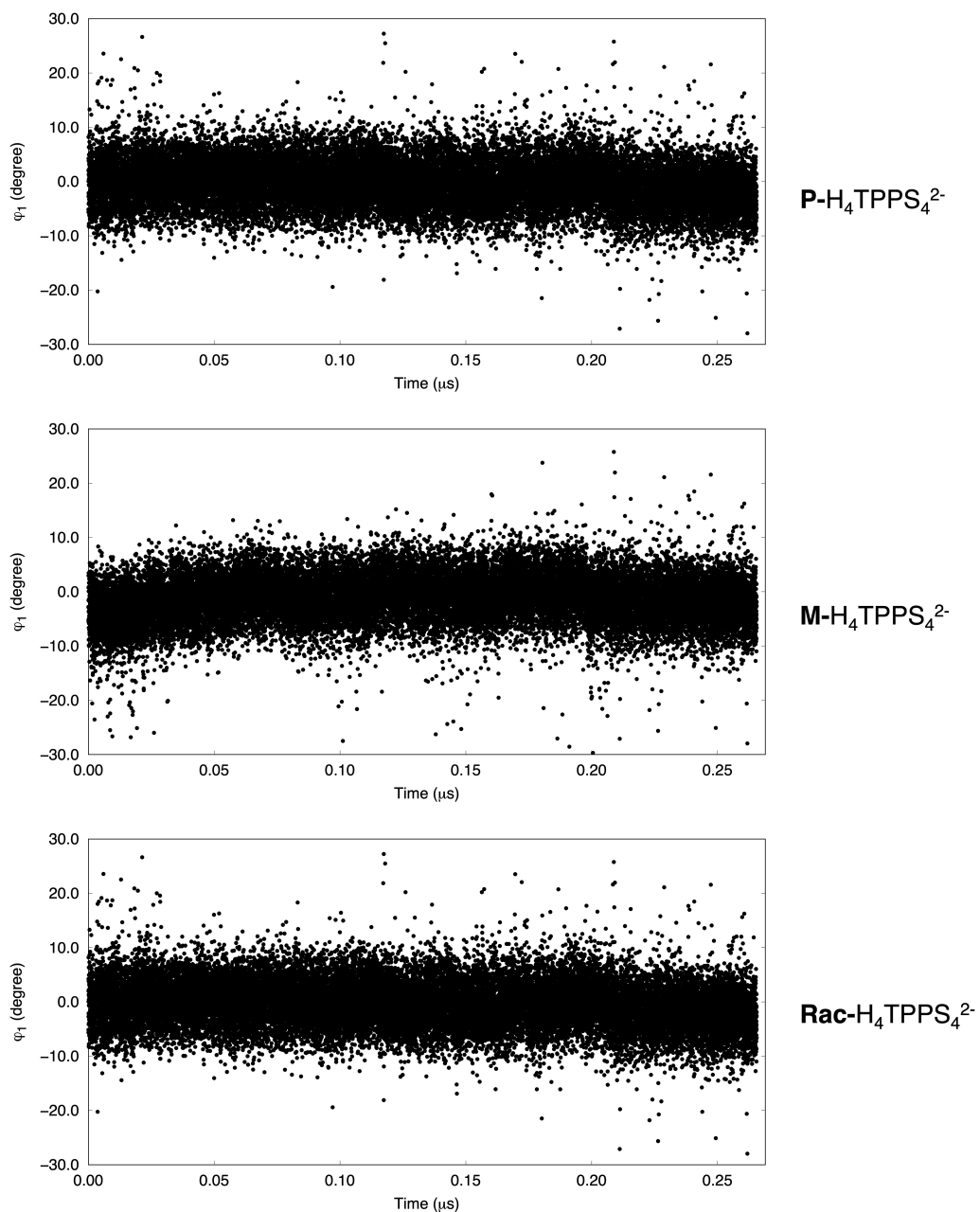
**Figure S2.** a) The four pyrrole torsions identifying the collective variables for the free-energy simulations. b)-c) The stacking distance and tilting angle defining the J-aggregate.



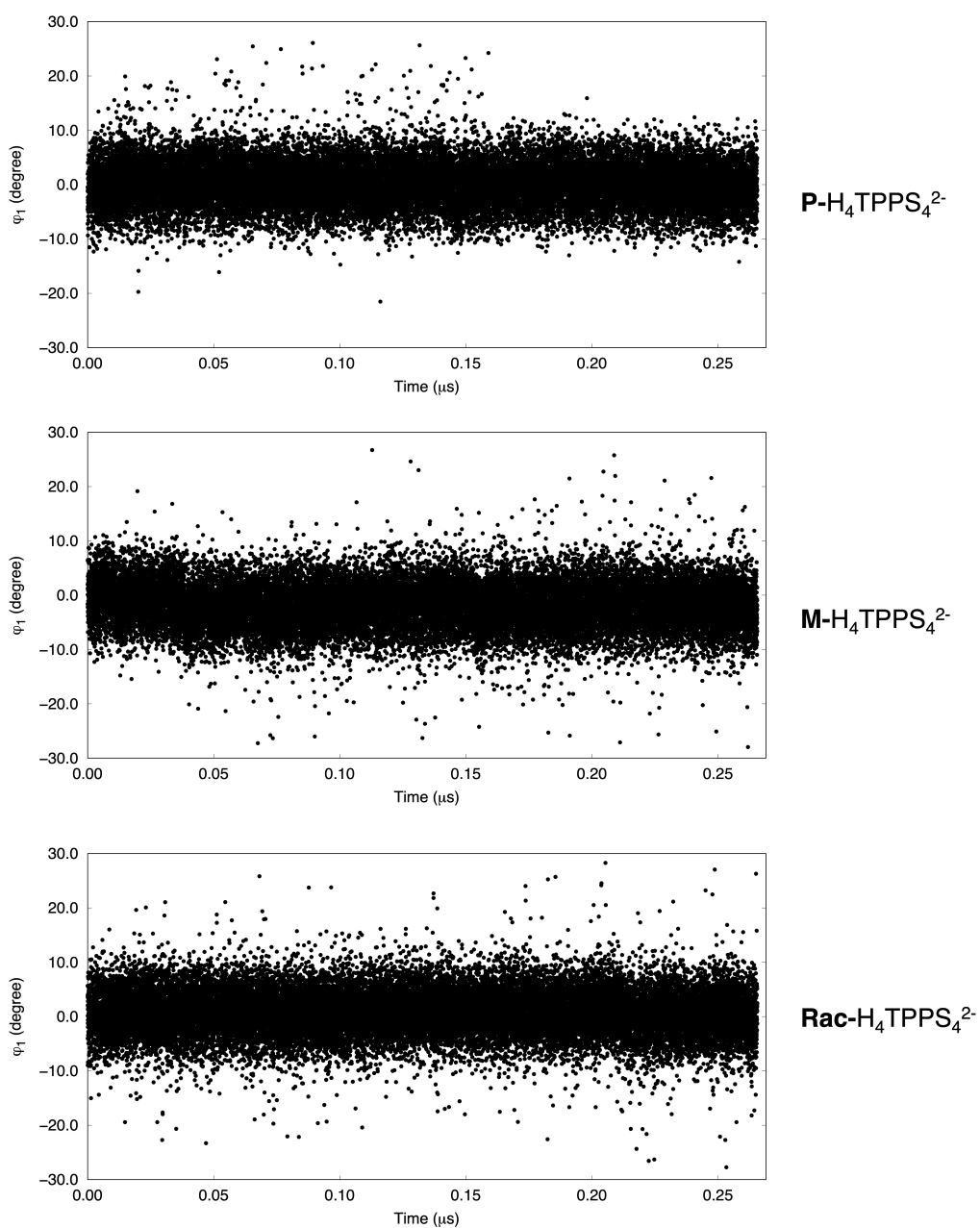
**Figure S3.** Variation of the representative dihedrals (pyrrole dihedral angles  $\phi_1$ ) of a **P-** H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup> (replica 1) **M-** H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup> (replica 2) and **Rac-** H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup> (replica 3) monomers as a function of the simulation progress, for the free-energy simulations.



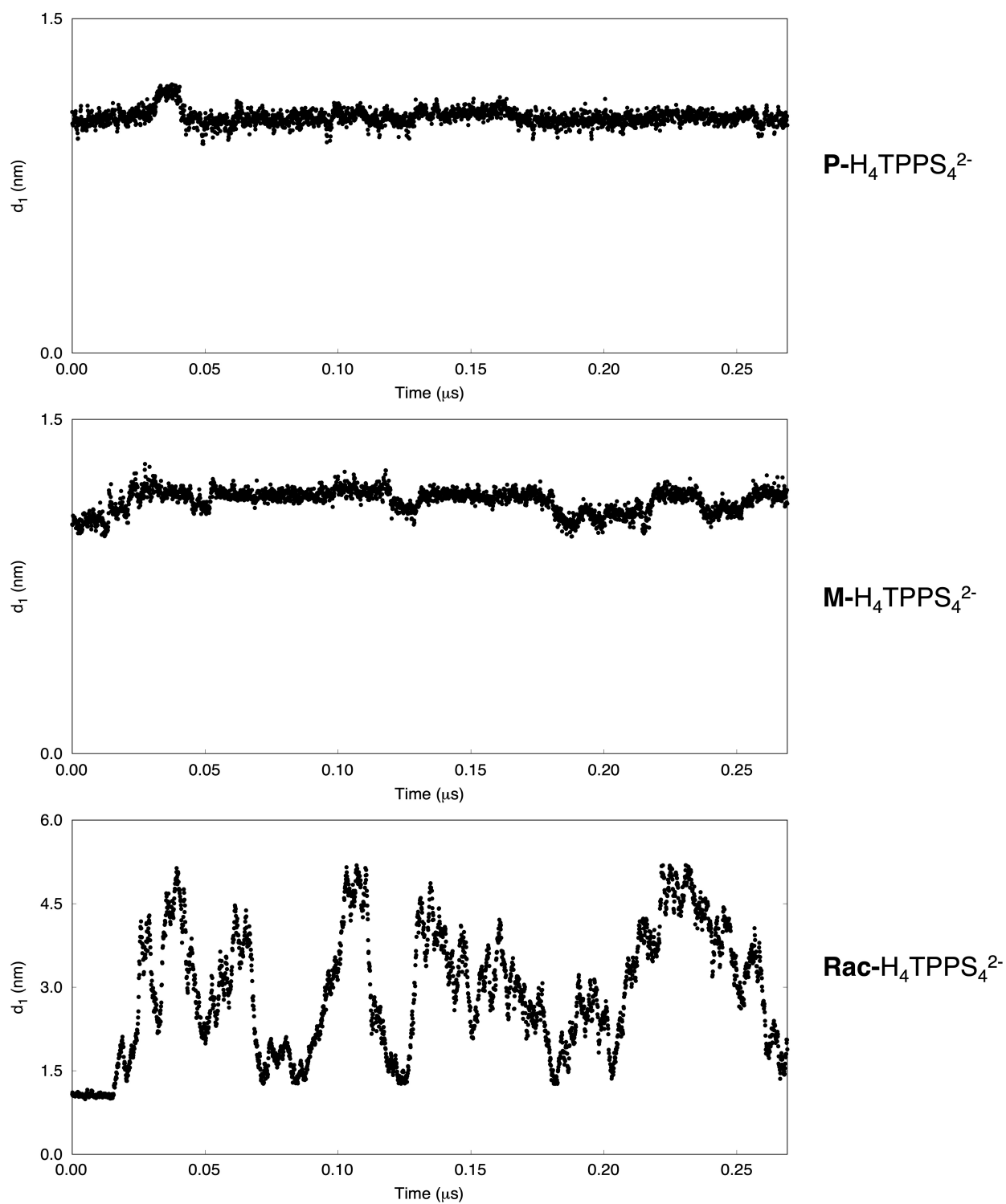
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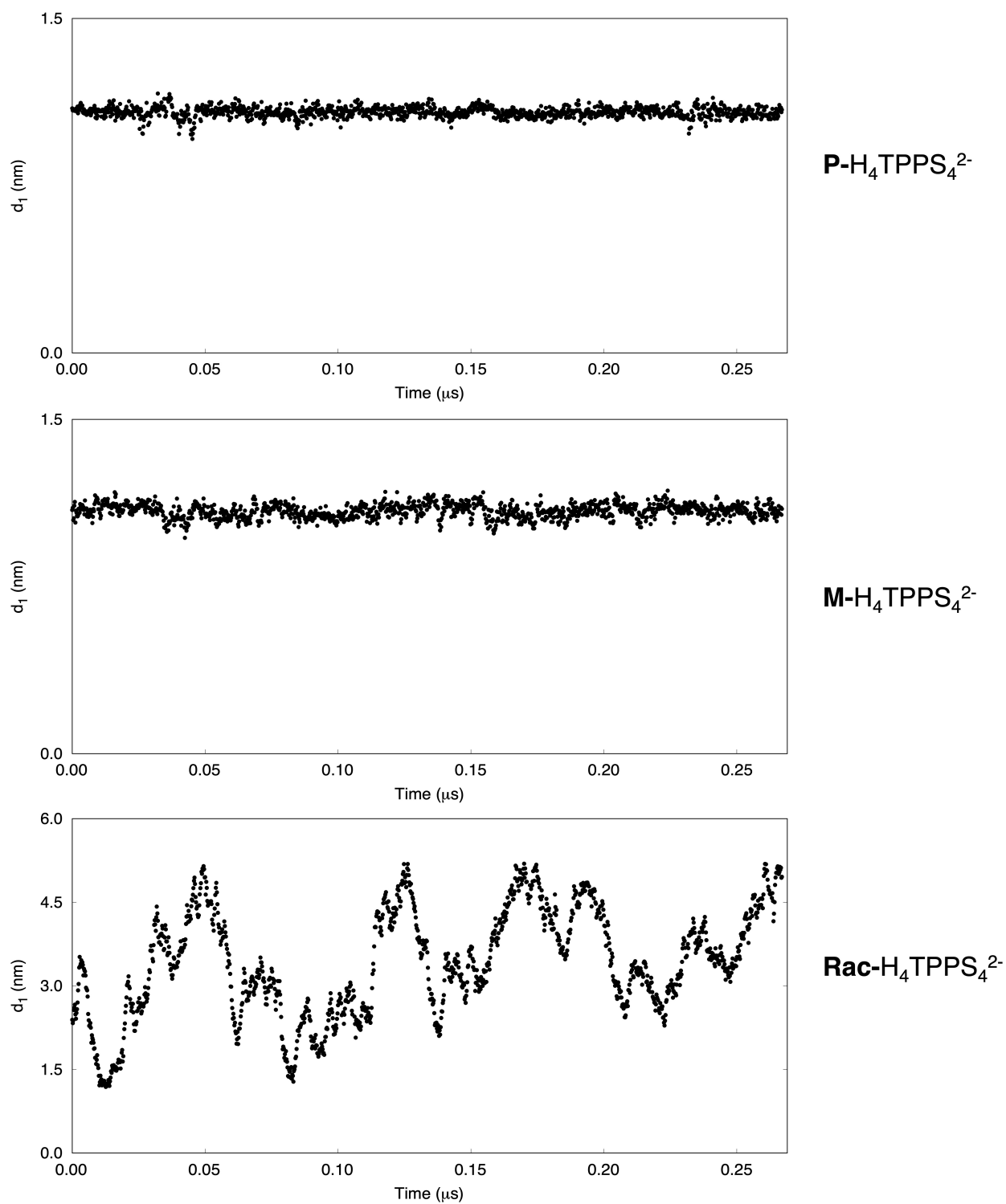
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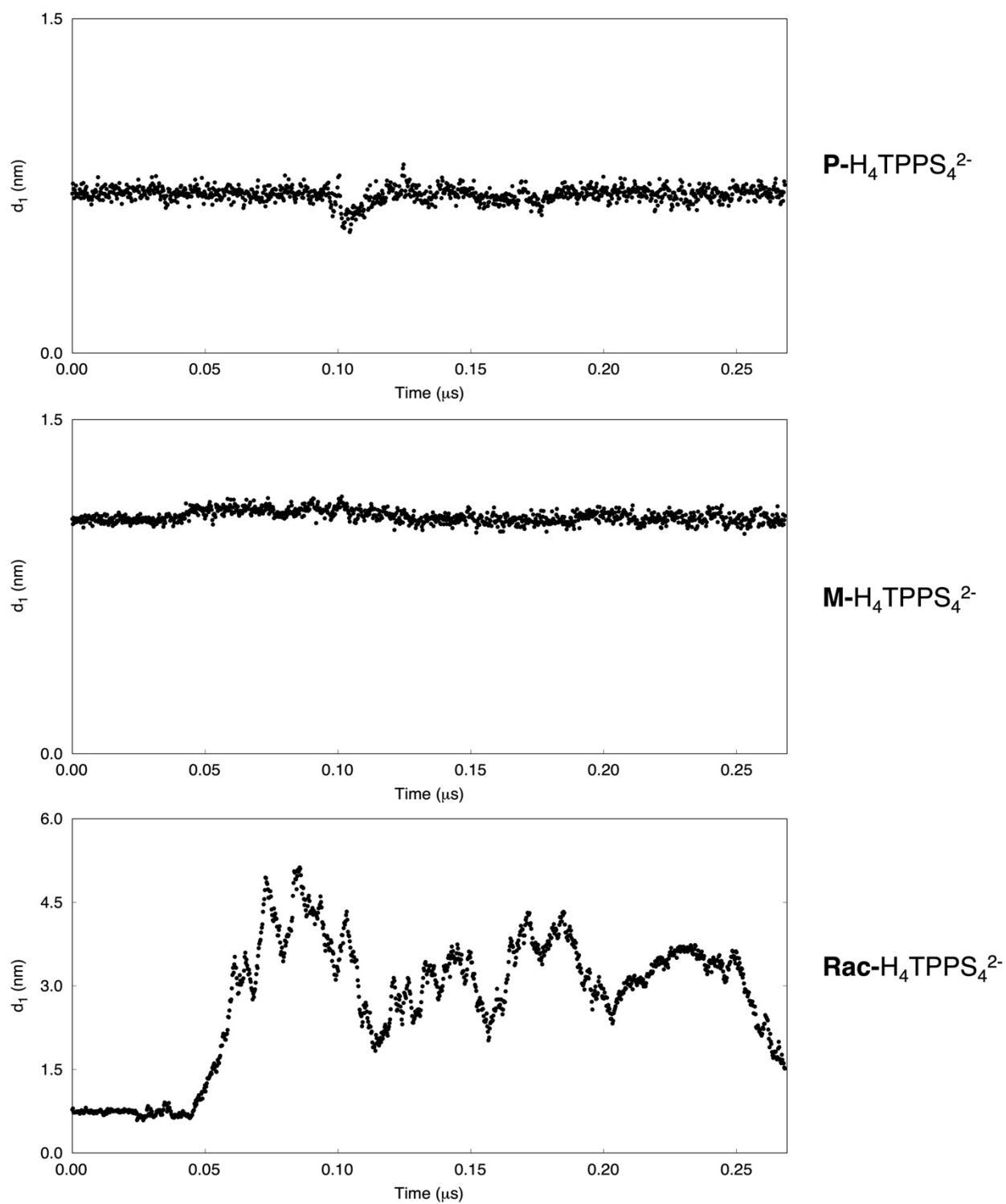


**Figure S7.** Variation of the representative distance between two adjacent porphyrins of a **P- $\text{H}_4\text{TPPS}_4^{2-}$** , **M- $\text{H}_4\text{TPPS}_4^{2-}$**  and **Rac- $\text{H}_4\text{TPPS}_4^{2-}$**  dimers as a function of the simulation progress, for the free-energy simulations.

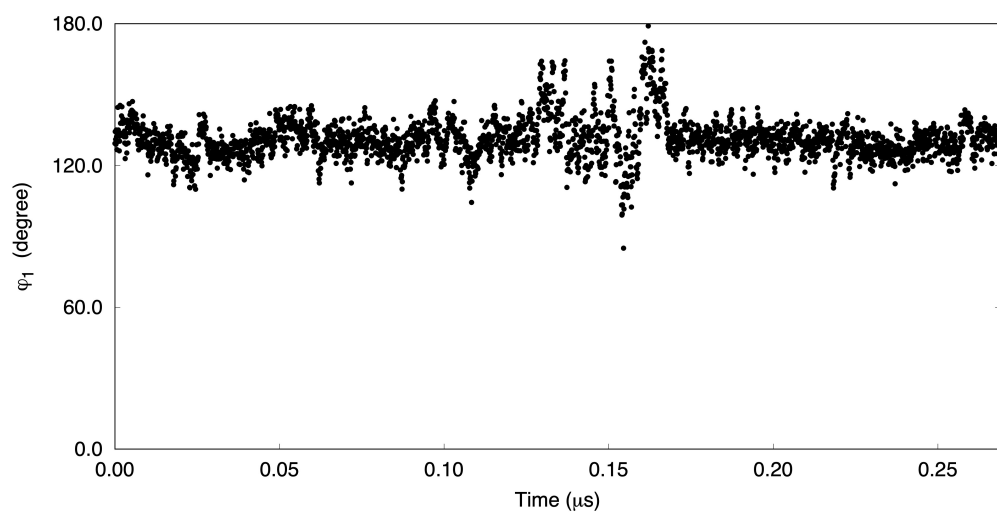


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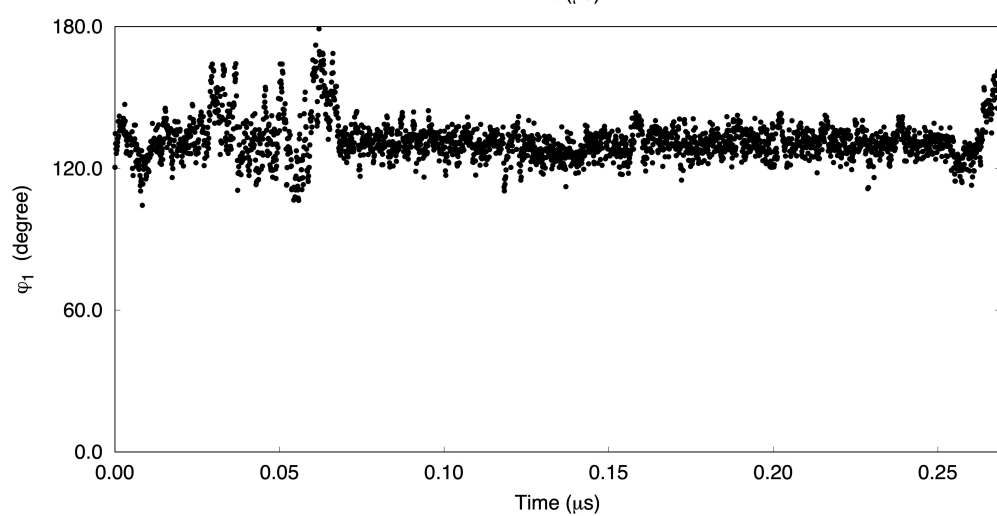




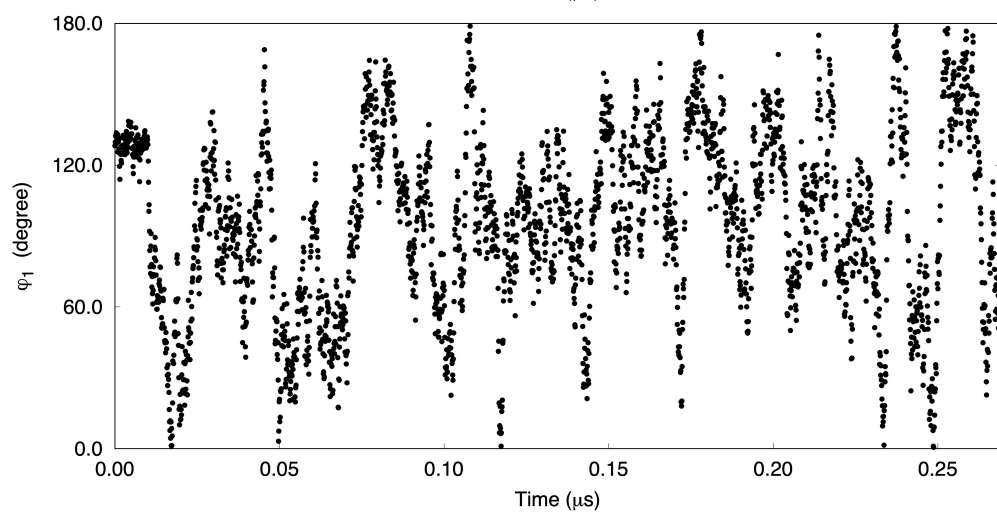
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**P-H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup>**

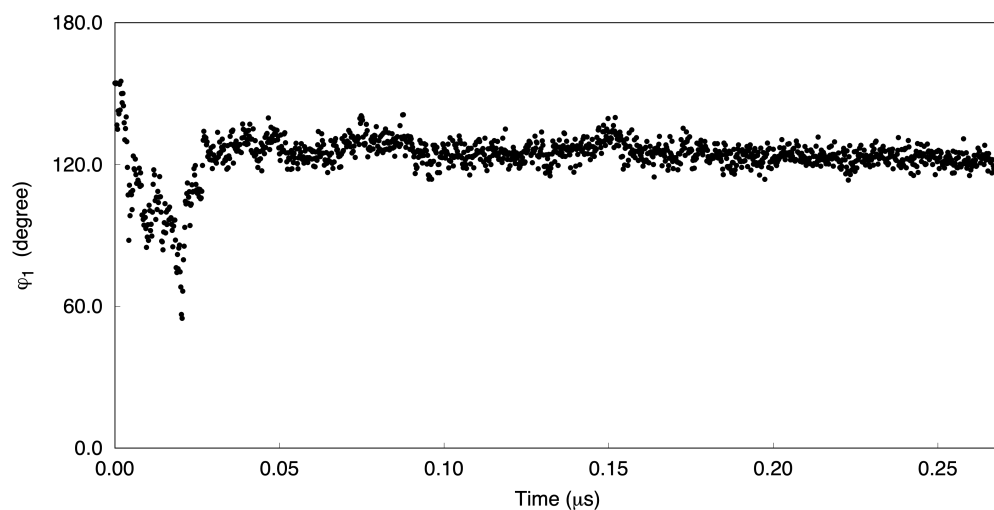


**M-H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup>**

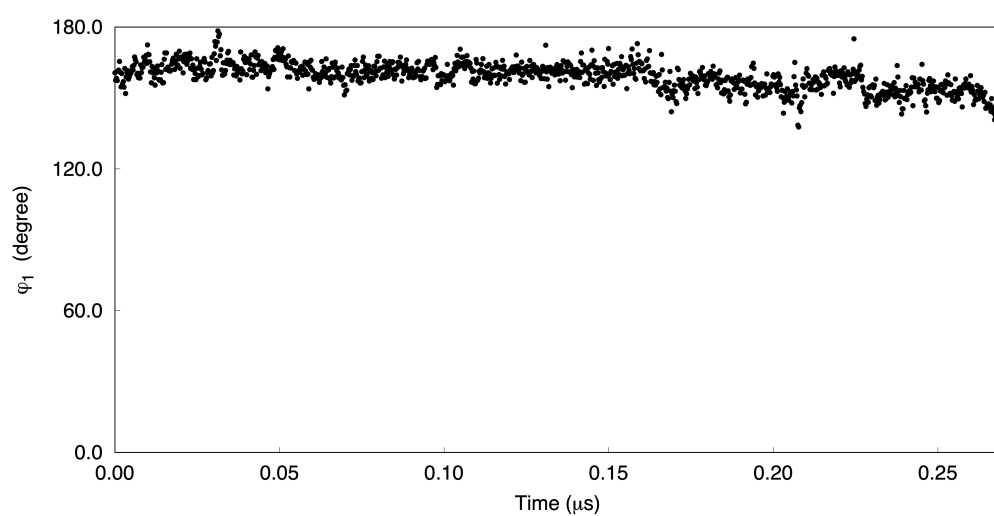


**Rac-H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup>**

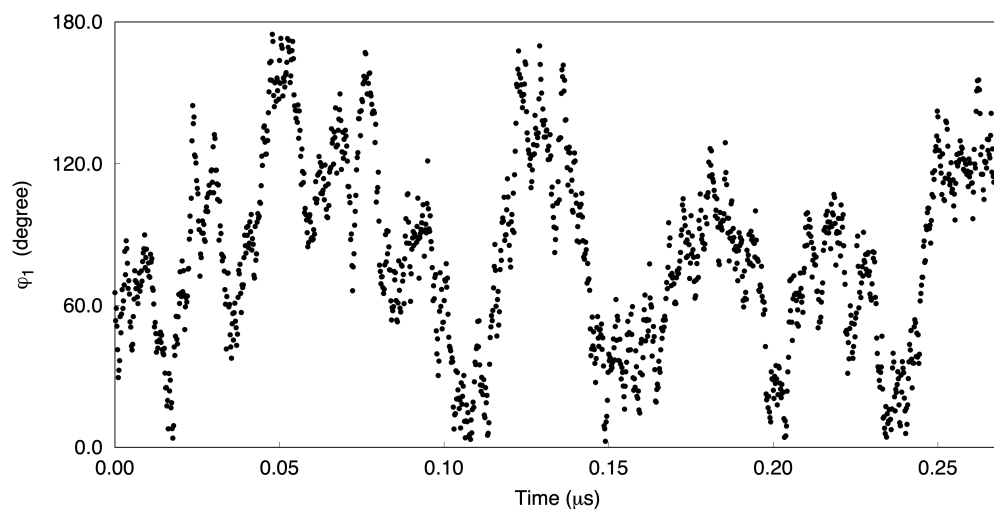
**Figure S10.** Variation of the representative tilting angle of a **P-** H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup> **M-** H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup> and **Rac-** H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup> dimers as a function of the simulation progress, for the free-energy simulations.



**P-H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup>**

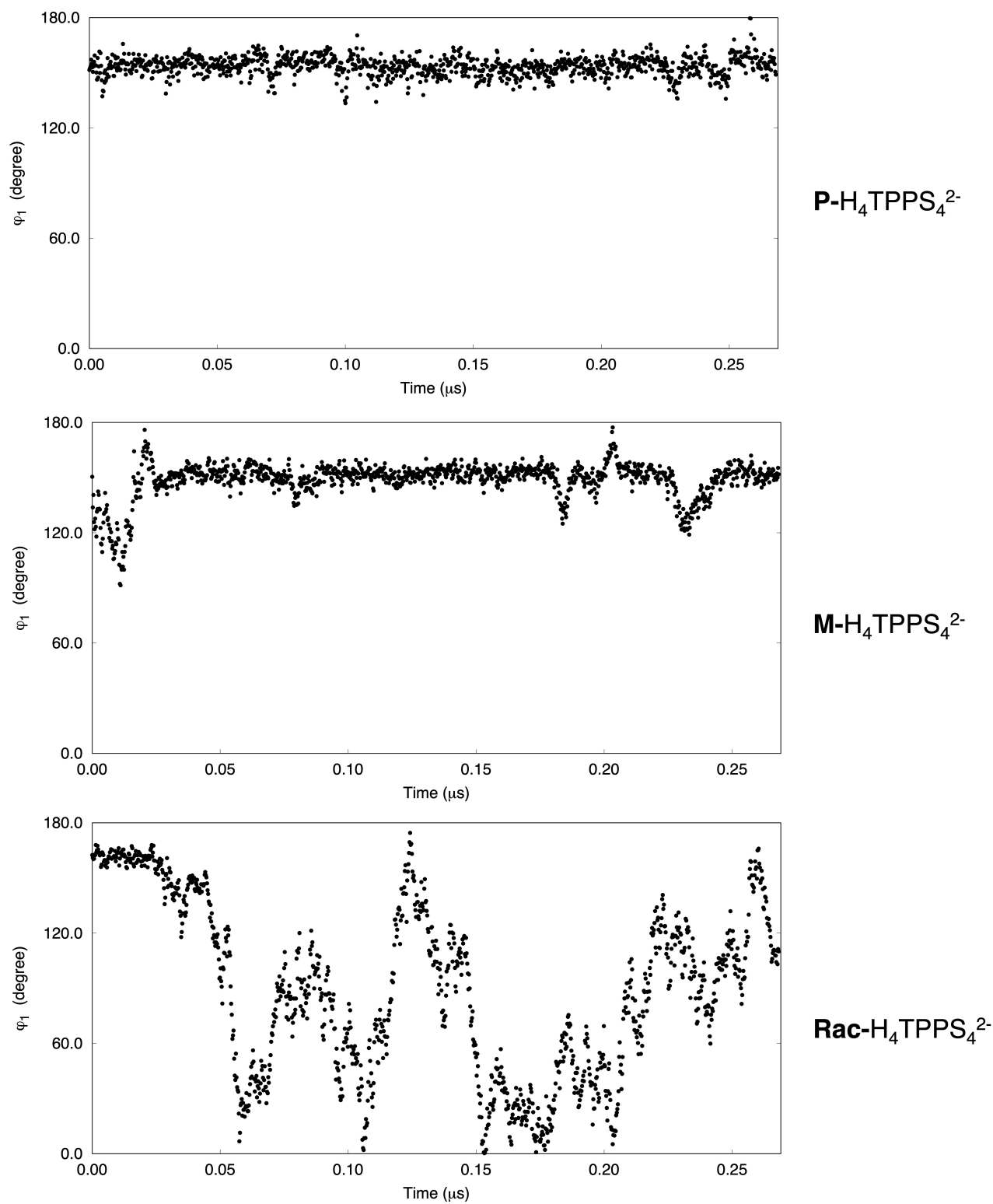


**M-H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup>**

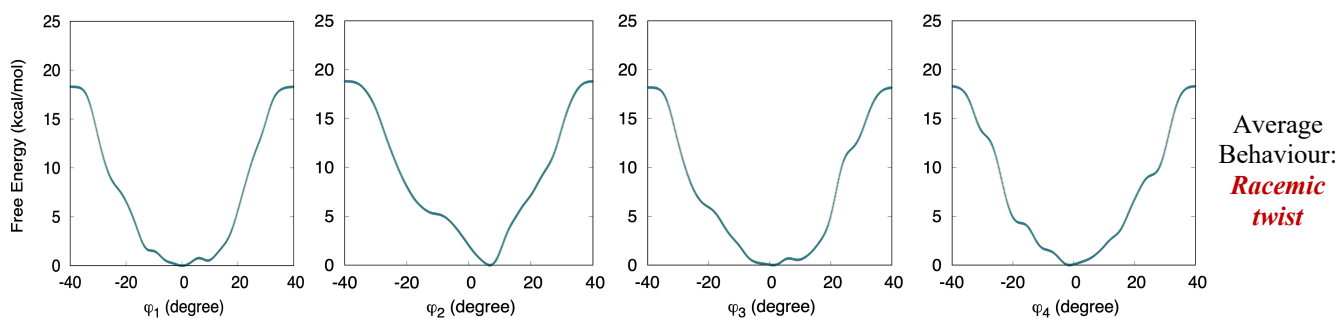


**Rac-H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup>**

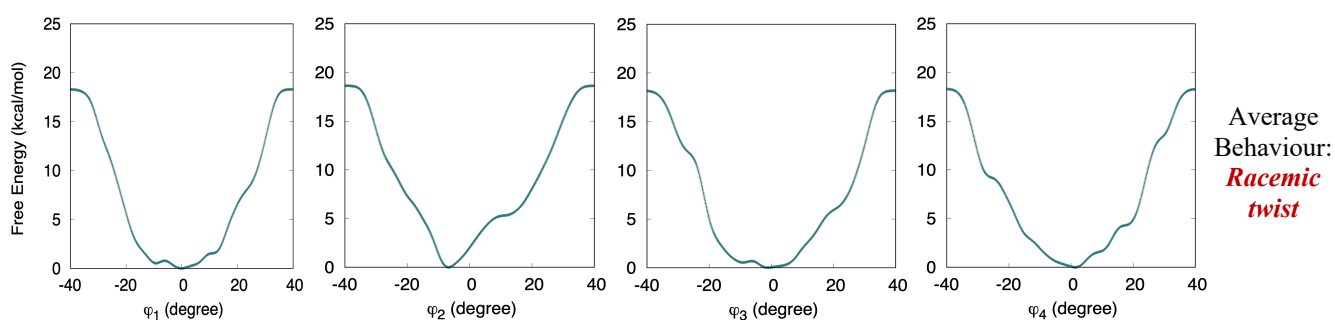
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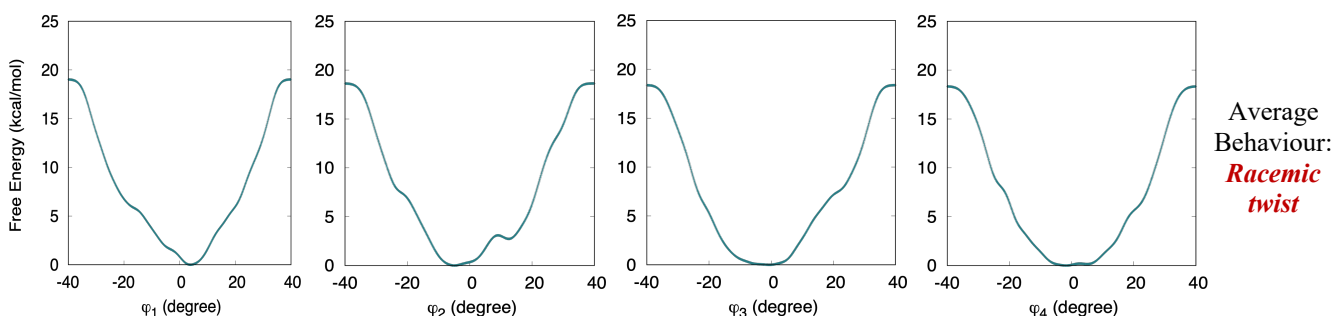
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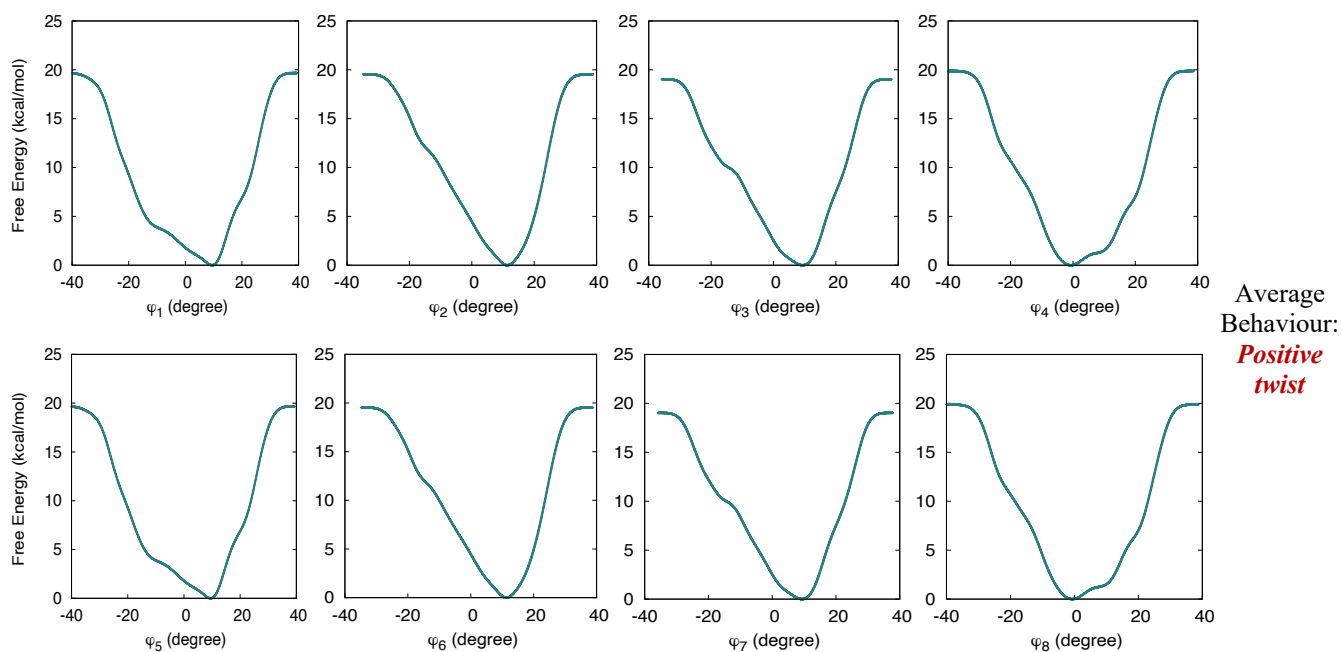
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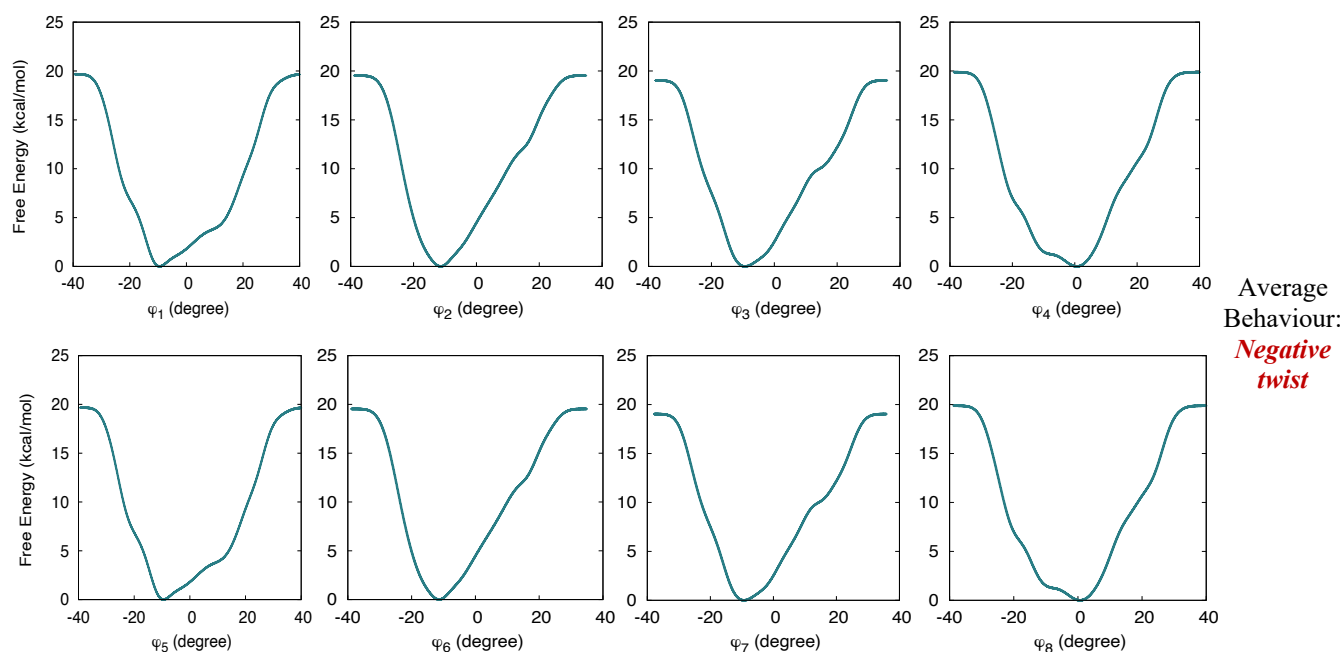
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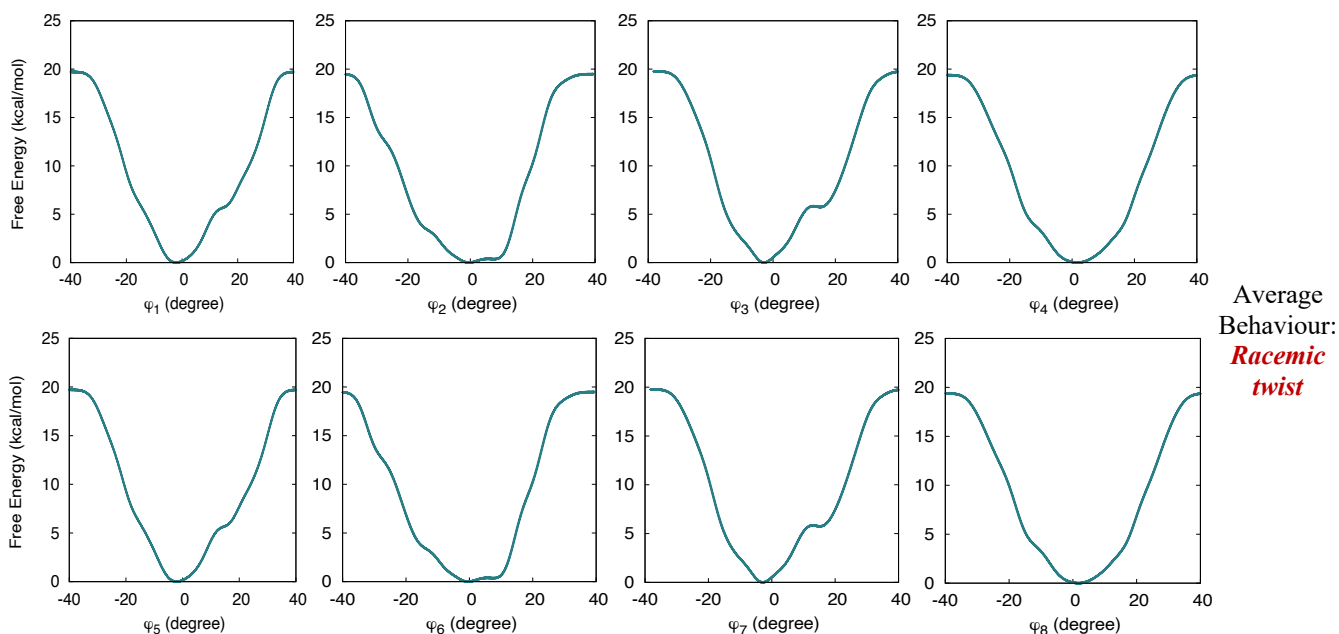
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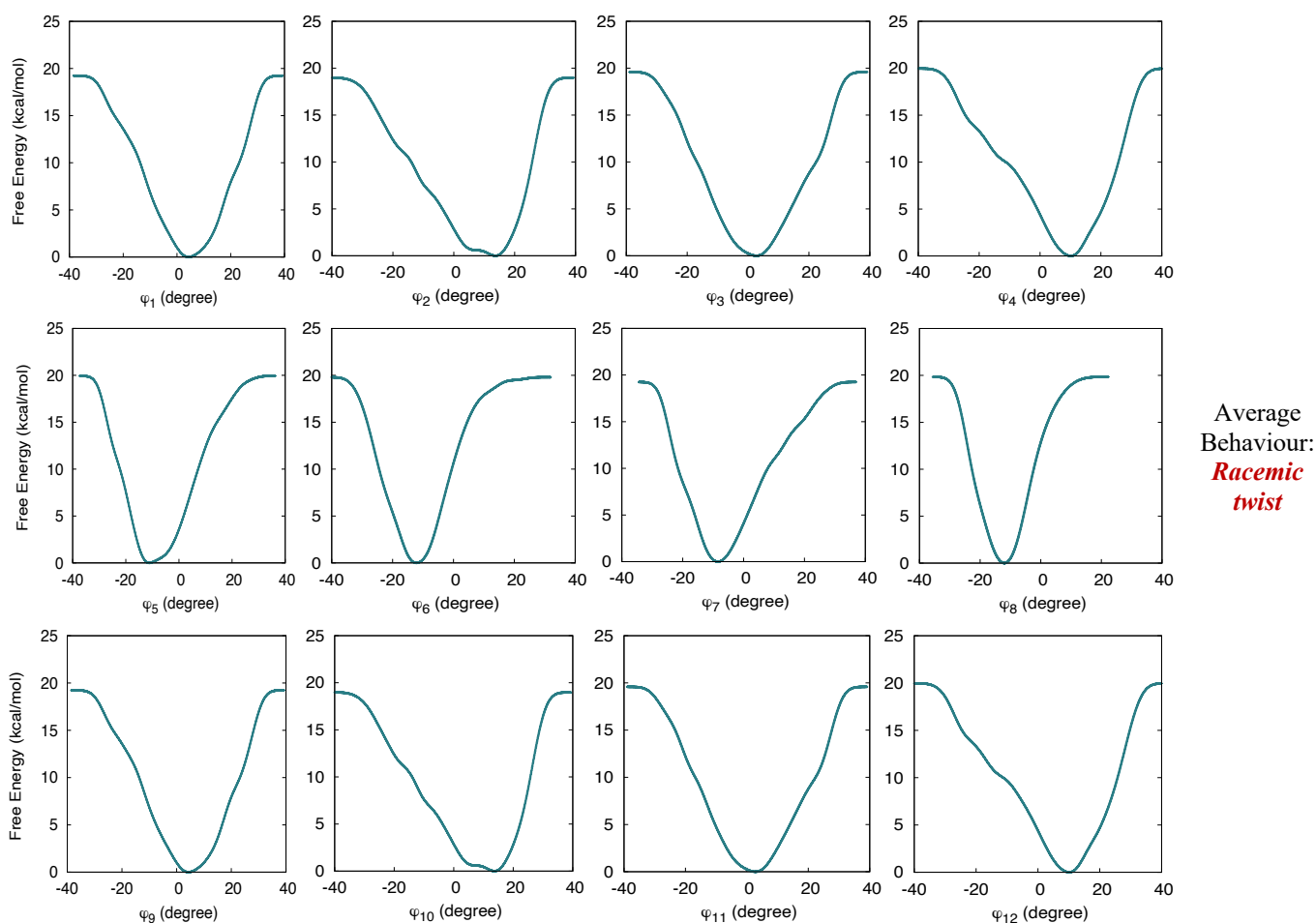
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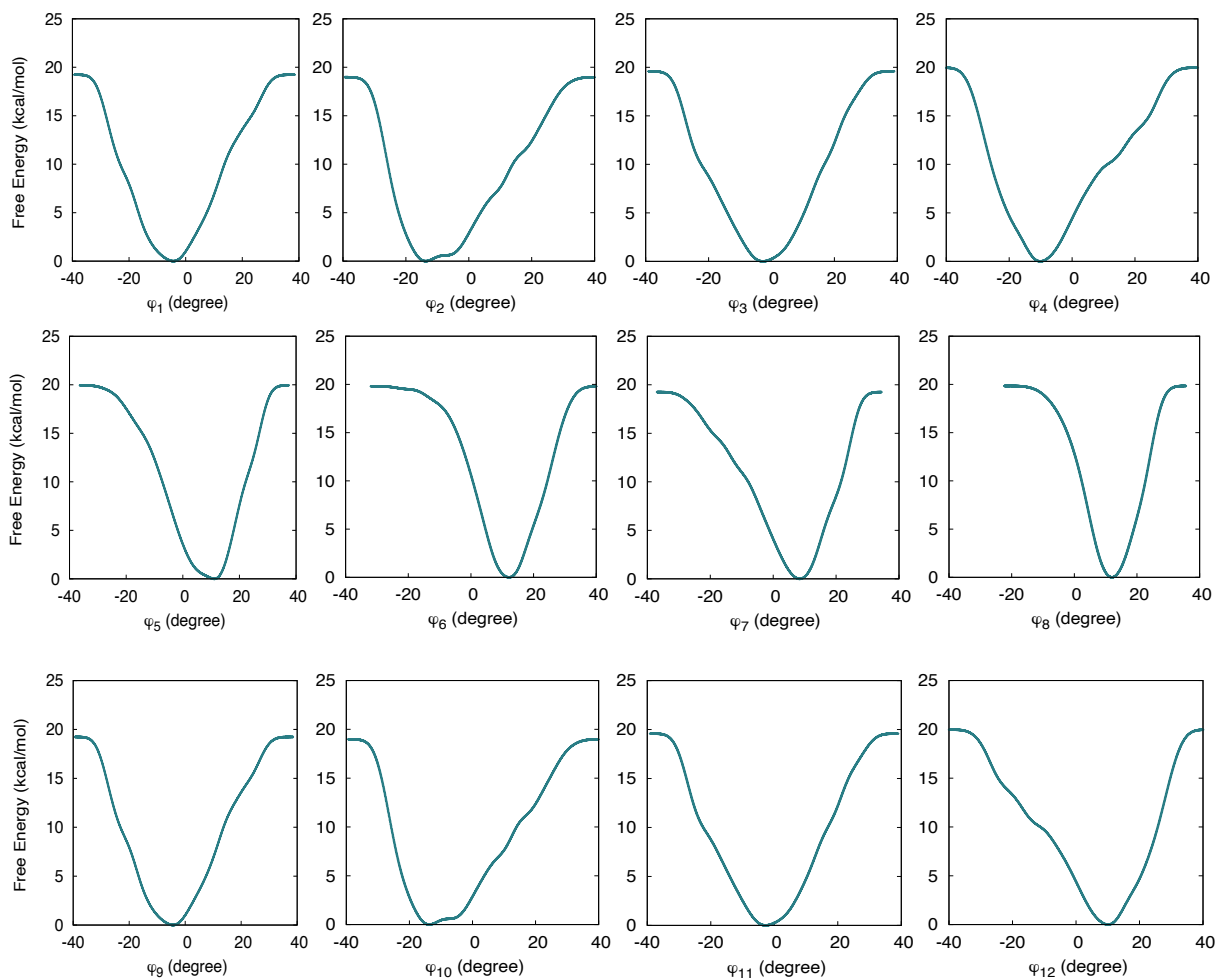
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**Figure S18.** Monodimensional free-energy profiles computed for the **Rac-H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup>** dimer within the PB-MetaD approach, as a function of the pyrrole dihedral angles  $\phi_1$ ,  $\phi_2$ ,  $\phi_3$ ,  $\phi_4$ . These maps have been constructed considering the data of **Rac-H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup>**, with two dihedral sulfonato-phenyl angles positive and two negative.

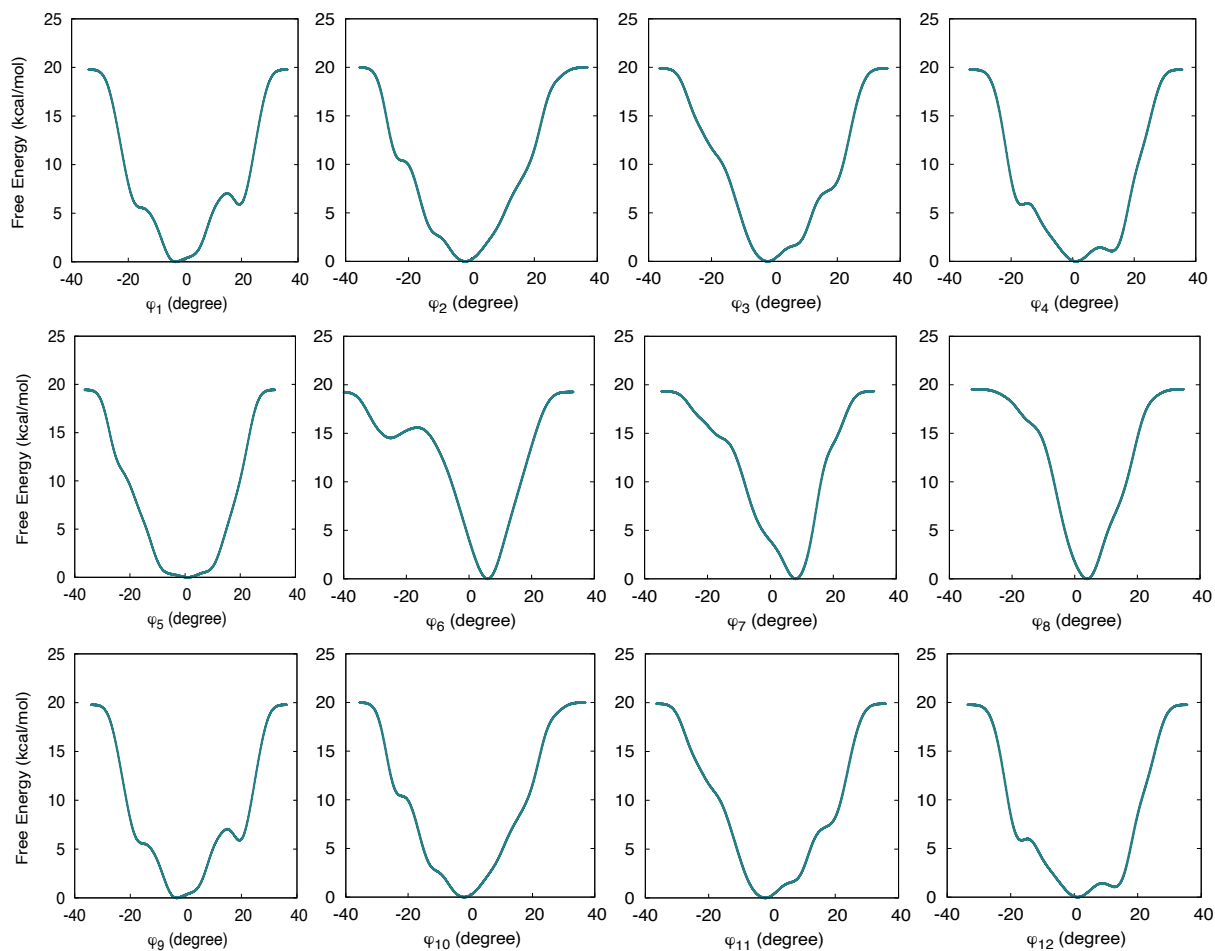


**Figure S19.** Mono-dimensional free-energy profiles computed for the **P-H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup>** trimer using the MW-MetaD approach, as a function of the pyrrole dihedral angles  $\phi_1$ ,  $\phi_2$ ,  $\phi_3$ ,  $\phi_4$ ,  $\phi_5$ ,  $\phi_6$ ,  $\phi_7$ ,  $\phi_8$ . These maps have been constructed considering the data of **M-H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup>**, having all the four sulfonato-phenyl dihedrals positive. a) Free energy profiles of external and b) internal porphyrin rings.



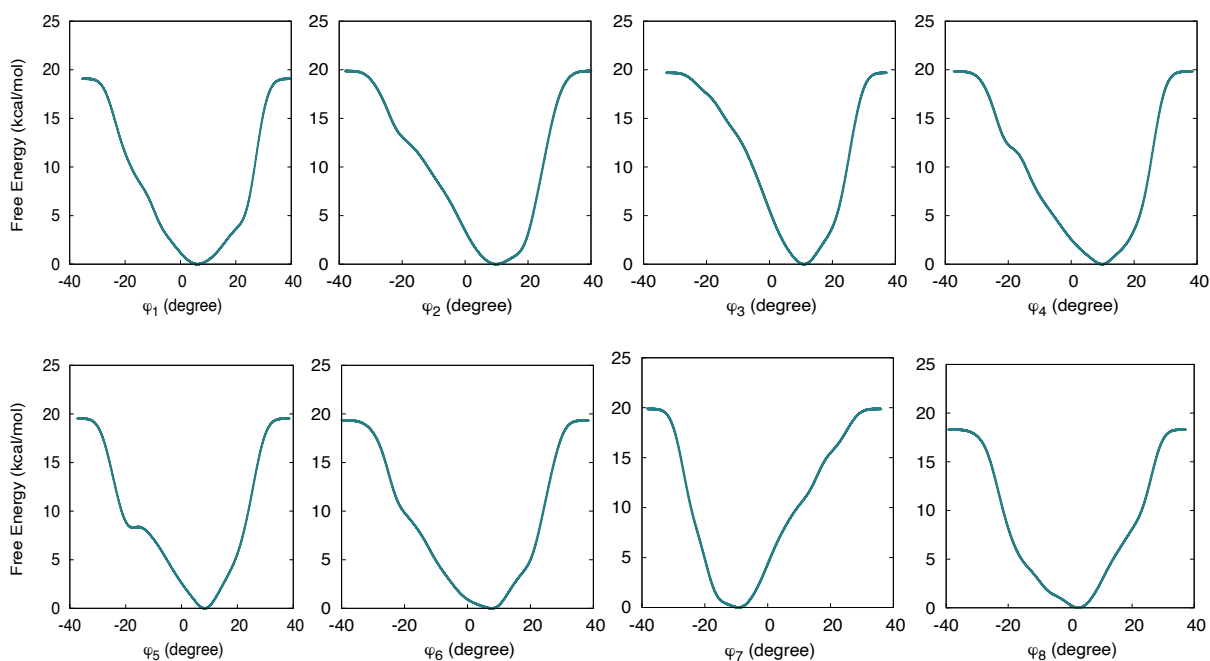
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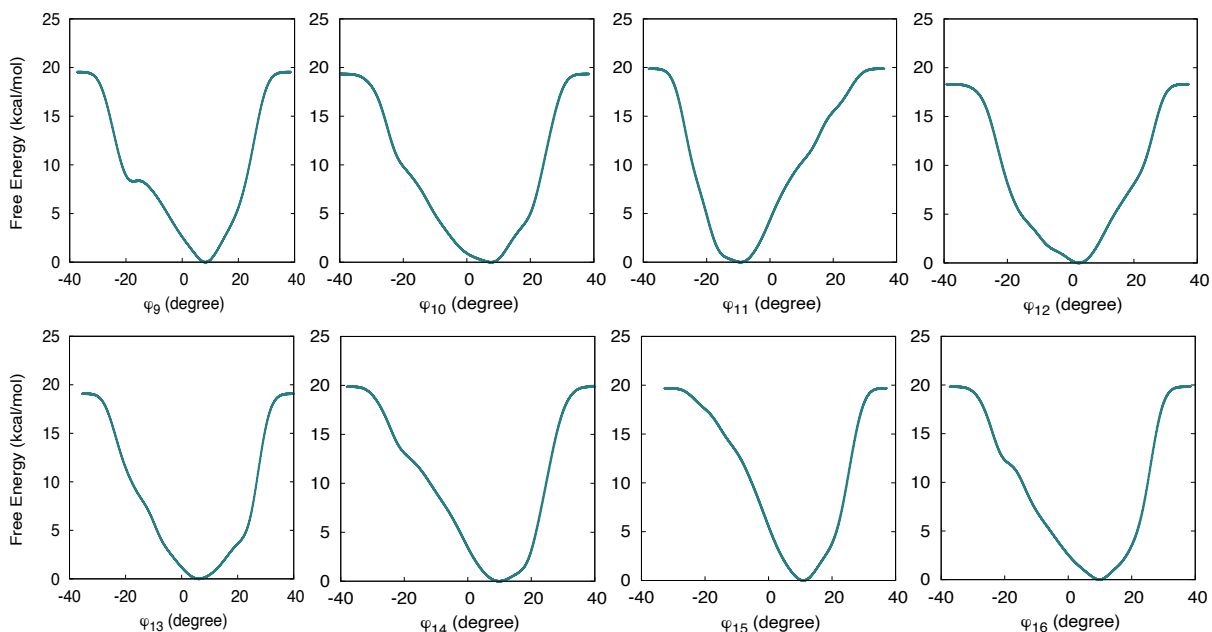


Average  
Behaviour:  
*Racemic*  
*twist*

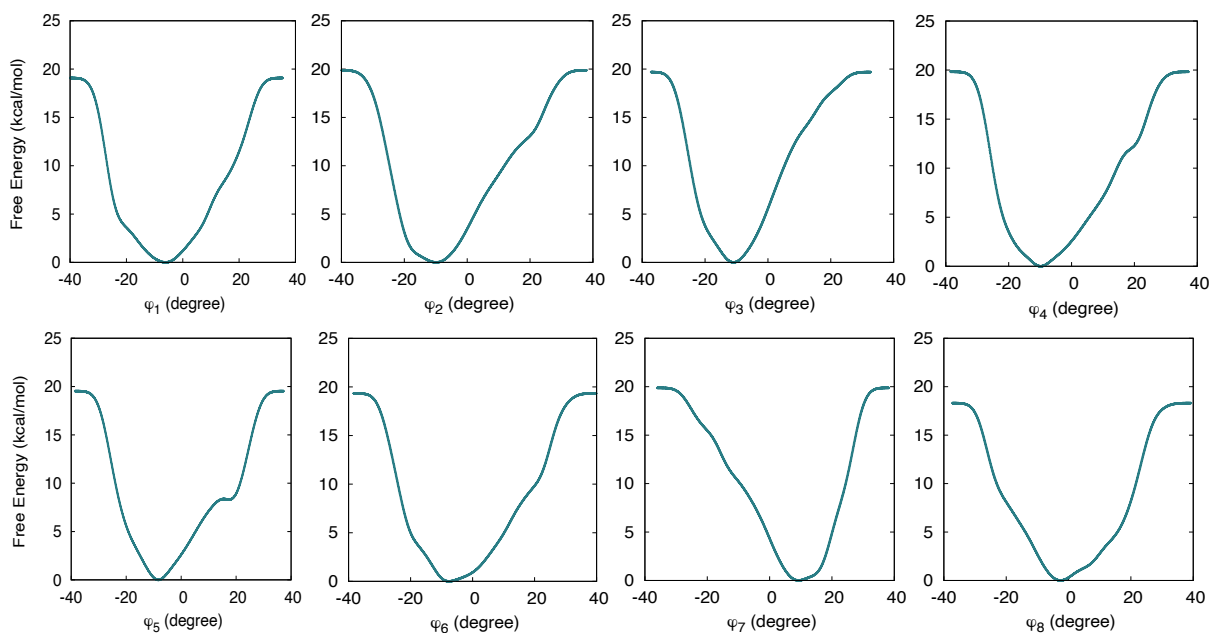
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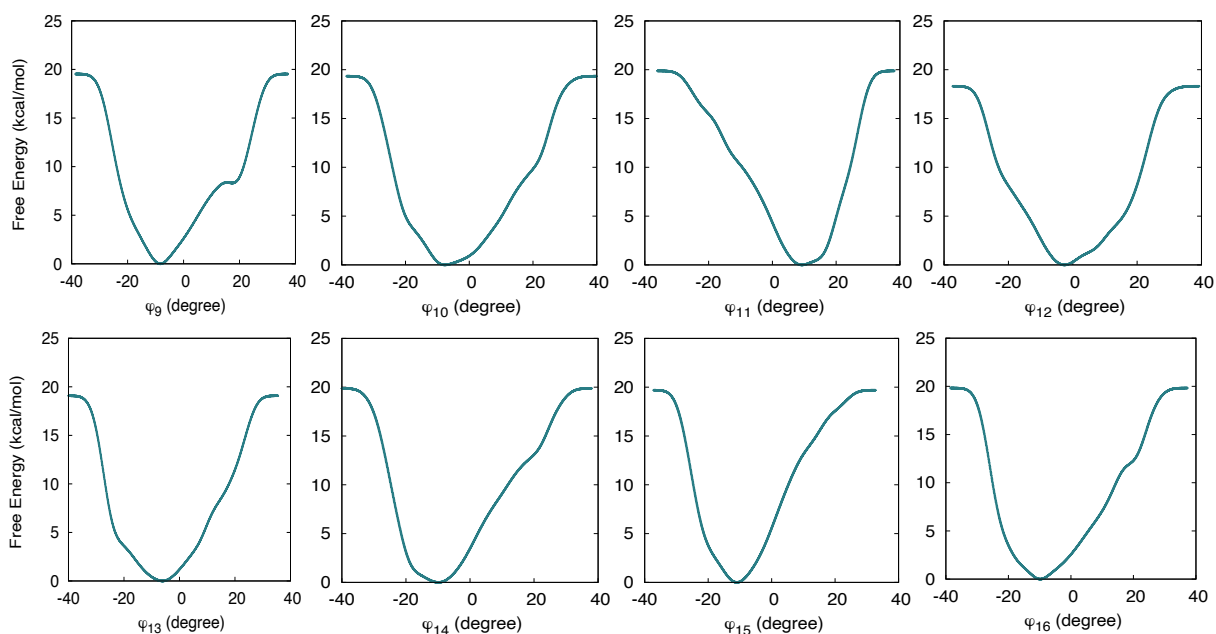
Average  
Behaviour:  
*Positive*  
*twist*



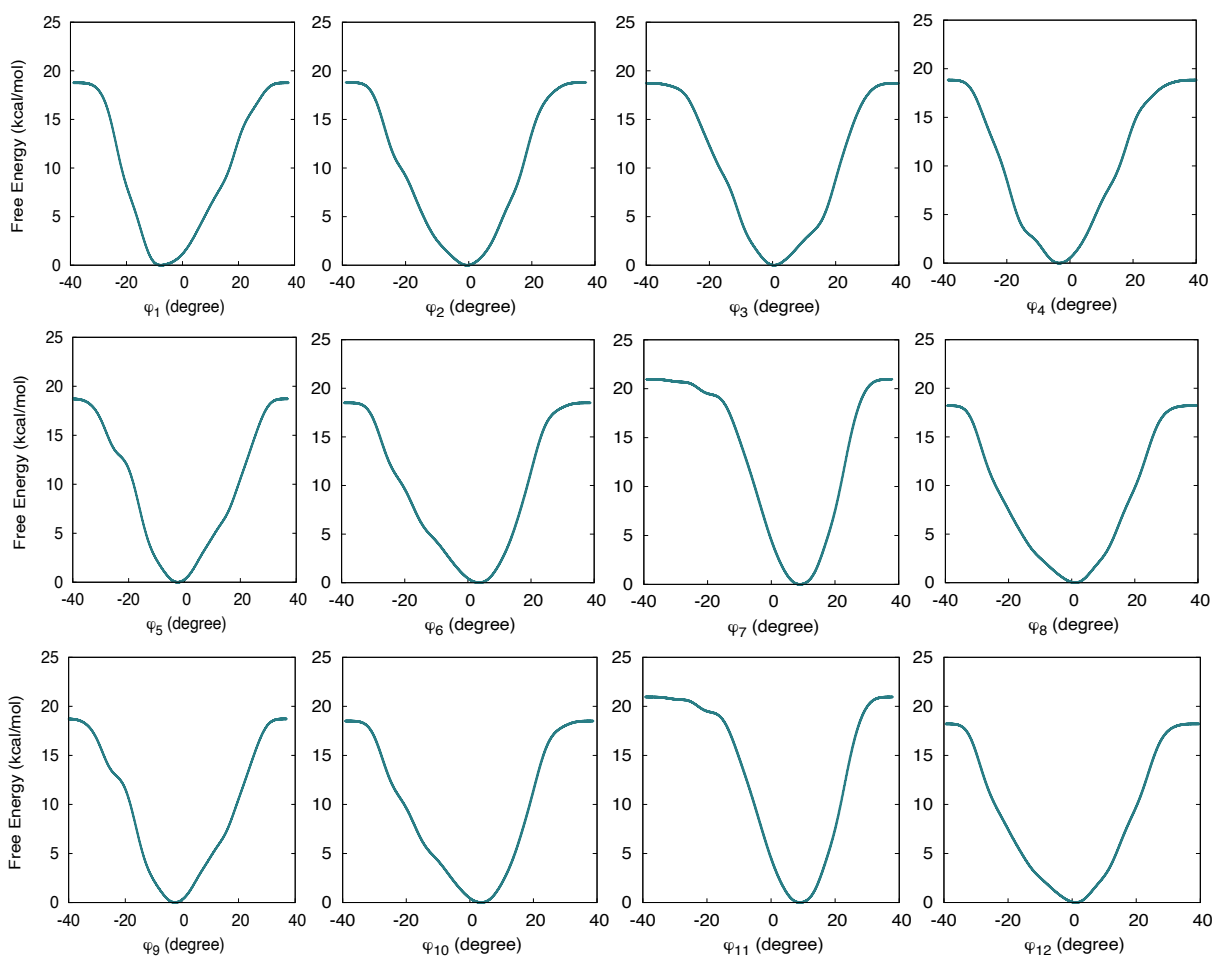
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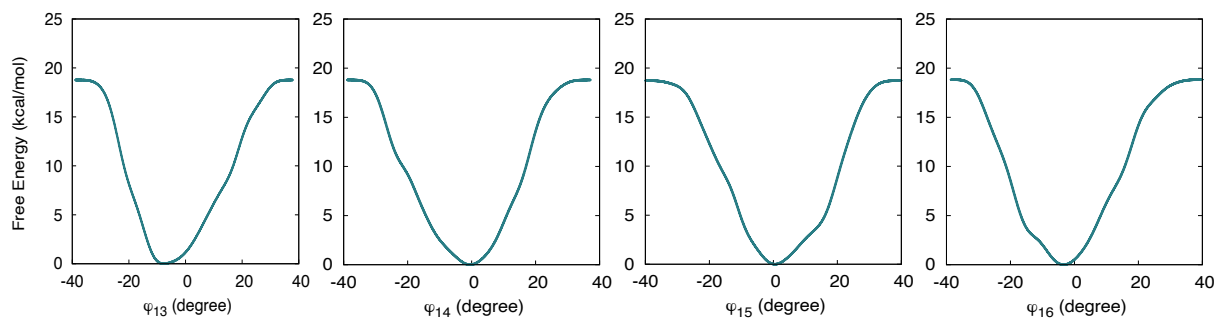
Average  
Behaviour:  
*Positive  
twist*



**Figure S23.** Mono-dimensional free-energy profiles computed for the  $\text{M-H}_4\text{TPPS}_4^{2-}$  tetramer using the MW-MetaD approach, as a function of the pyrrole dihedral angles  $\phi_1, \phi_2, \phi_3, \phi_4, \phi_5, \phi_6, \phi_7, \phi_8$ . These maps have been constructed considering data of  $\text{P-H}_4\text{TPPS}_4^{2-}$ , that is structure that have all four dihedral sulfonato-phenyl angles negative. a) Free energy profiles of external porphyrin rings and b) free energy profiles of internal porphyrin rings.



Average  
Behaviour:  
*Negative  
twist*



**Figure S24.** Mono-dimensional free-energy profiles computed for the **Rac-H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup>** tetramer using the MW-MetaD approach, as a function of the pyrrole dihedral angles  $\phi_1, \phi_2, \phi_3, \phi_4, \phi_5, \phi_6, \phi_7, \phi_8$ . These maps have been constructed considering data of P-H<sub>4</sub>TPPS<sub>4</sub><sup>2-</sup>, that is structure that have all four dihedral sulfonato-phenyl angles positive. a) Free energy profiles of external porphyrin rings and b) free energy profiles of internal porphyrin rings.