Electronic Supporting Information for

Molecular Simulations of Cytochrome c Adsorption on Positively Charged Surfaces: The Influence of Anion Type and Concentration

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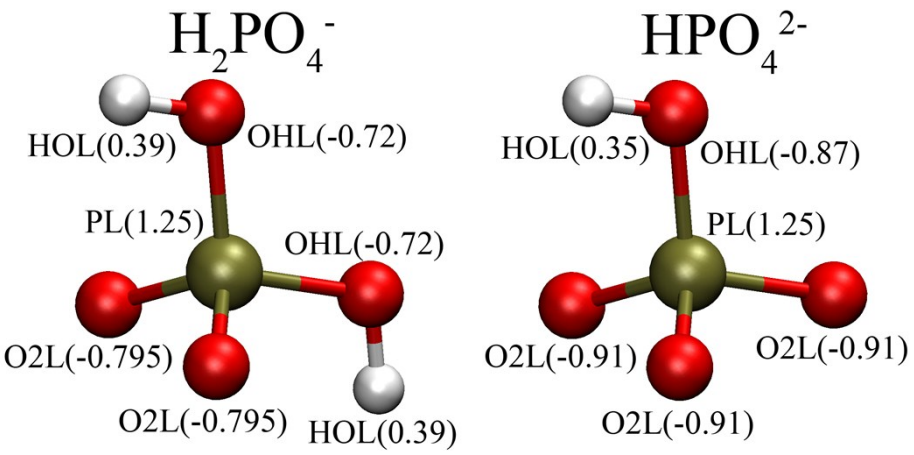

Figure S1: CHARMM atom-type and fractional charge assigned to each atom in phosphate ion. The charges are obtained from a structure optimized in gas phase at the B3LYP/6-31+G* level; atoms of the same type are restrained to have identical charges. Charge assignment for dihydrogen phosphate is adopted from reference.[1]

A full list of force field parameters for phosphate[2-3] (Tables S1-S4)

Table S1: Non-bonded parameters for phosphate, taken from existing parameters in the CHARMM force field.

Atom type	σ (nm)	ε (kJ·mol^{-1})
PL	0.38309	2.44764
O2L	0.30291	0.50208
OHL	0.31538	0.63639
HOL	0.04000	0.19246

Table S2: Bonded parameters for V^{bond}, taken from existing parameters in the CHARMM force field.

Atoms i and j		b_0 (nm)	k_b (kJ·mol^{-1}·nm^{-2})
PL	O2L	0.148	485344.0
PL	OHL	0.159	198321.6
OHL	HOL	0.096	456056.0

Table S3: Bonded parameters for V^{angle}, taken from existing parameters in the CHARMM force field. The underlined parameters are adopted from reference.[2]

Atoms i, j and k			θ_0 (deg)	k_θ (kJ·mol^{-1})	r_{13} (nm)	k_{UB} (kJ·mol^{-1})
PL	OHL	HOL	115.0	251.04	0.23	33472.0
O2L	PL	O2L	120.0	1004.16	0.0	0.0
OHL	PL	O2L	108.23	827.5952	0.0	0.0
OHL	PL	OHL	104.0	827.5952	0.0	0.0

Table S4: Bonded parameters for $V^{dihedral}$, taken from existing parameters in the CHARMM force field.

Atoms i, j, k and l				φ_s (deg)	k_φ (kJ·mol^{-1})	multiplicity
O2L	PL	OHL	HOL	0.0	1.2552	3
OHL	PL	OHL	HOL	0.0	1.2552	3

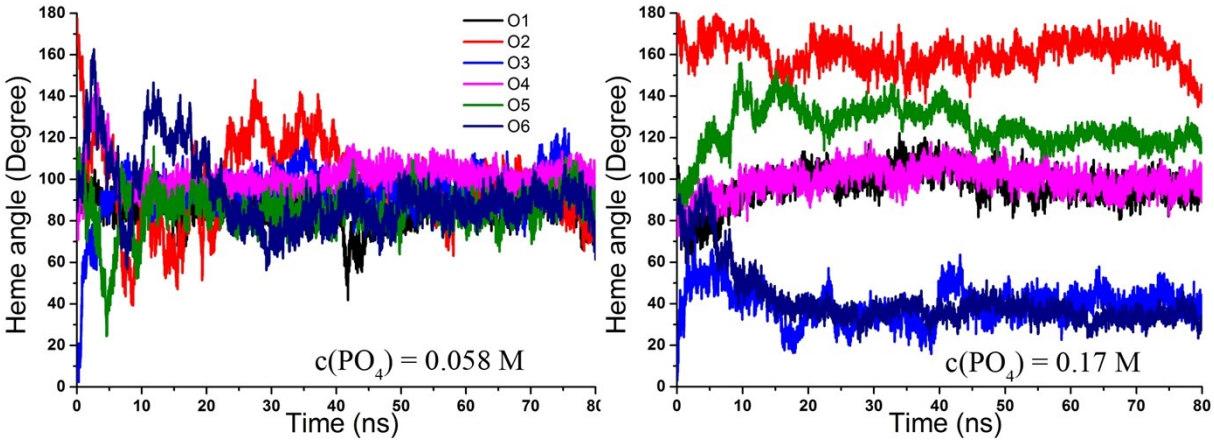

Figure S2. Evolution of the tilt angle of the heme prosthetic group for Cyt-c adsorbed on the NH_2-SAM surface under different phosphate concentrations.

Table S5. Interaction Energies[a] between Cyt-c and the NH_2-SAM Surface

System	Energy	O1	O2	O3	O4	O5	O6
0.058 M	E_{vdw}	−75 ± 17	−84 ± 15	−43 ± 21	**−140 ± 16**	−28 ± 13	−46 ± 14
	E_{ele}	**−397 ± 58**	−228 ± 52	−213 ± 77	−51 ± 41	−136 ± 41	−132 ± 80
0.17 M	E_{vdw}	−31 ± 17	−25 ± 9	−96 ± 20	**−162 ± 23**	−44 ± 11	−92 ± 17
	E_{ele}	**−189 ± 57**	−32 ± 56	−132 ± 50	−44 ± 26	−76 ± 33	−78 ± 48

[a]The units of the energies are kJ mol^{-1}.

References

(1) Yang, W.; Gao, Y. Q.; Cui, Q.; Ma, J.; Karplus, M. The missing link between thermodynamics and structure in F1-ATPase. *Proc. Natl. Acad. Sci. U. S. A.* **2003,** *100*, 874-879.

(2) Vanommeslaeghe, K.; Hatcher, E.; Acharya, C.; Kundu, S.; Zhong, S.; Shim, J.; Darian, E.; Guvench, O.; Lopes, P.; Vorobyov, I., et al. CHARMM general force field: A force field for drug-like molecules compatible with the CHARMM all-atom additive biological force fields. *J. Comput. Chem.* **2010,** *31*, 671-690.

(3) Mallajosyula, S. S.; Guvench, O.; Hatcher, E.; MacKerell, A. D. CHARMM Additive All-Atom Force Field for Phosphate and Sulfate Linked to Carbohydrates. *J. Chem. Theory Comput.* **2011,** *8*, 759-776.