Storage, transport, release: heme versatility in nitrite reductase electron transfer studied by molecular dynamics simulations

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Nitrite reductases play an important role in the bacterial assimilation of nitrogen and the global nitrogen cycle. They use a notably large number of six electrons to reduce nitrite to ammonia. Applying molecular dynamics simulations of the thermodynamic integration type [1,2], we study the energetics and kinetics of electron transfer through the nitrite reductase enzyme of *Sulfospirillum deyleianum*, *Wolinella succinogenes* and *Campylobacter jejuni*. In all of these five-heme proteins, the storage of an even number of electrons within a monomeric chain is thermodynamically favoured. Kinetically, electrons are usually transferred in pairs. Although the free energy landscape for charge transfer varies significantly from organism to organism, the heme cofactor closest to the interface of a protein dimer always exhibits a particularly low ΔG, suggesting that protein dimerization is functional.

[1] S. Krapf, T. Koslowski, T. Steinbrecher, The thermodynamics of charge transfer in DNA photolyase: using thermodynamic integration calculations to analyse the kinetics of electron transfer reactions, Phys. Chem. Chem. Phys. 12, 9516-9525 (2010)

[2] F. Burggraf, T. Koslowski, Charge transfer through a cytochrome multi-heme chain: Theory and simulation, BBA Bioenergetics 1837, 186-192 (2014)