Proteins with non-heme Fe

- 1. Proteins where Fe is exclusively bound to aminoacids (and/or H_2O , OH^- , O^{2-})
- 2. Proteins that contain Fe–S centers



Hemerythrin homo-octamer with a single monomer highlighted in yellow. Each subunit has a four- α -helix fold binding a binuclear

iron center.



Unlike hemoglobin, most hemerythrins lack cooperative binding to oxygen, making it roughly 1/4 as efficient as hemoglobin

The di-iron active site of hemerythrin before and after oxygenation

-0,



deoxyhemerythrin

Deoxyhemeritrin

Colorless 2 Fe(II) h.s. (S = 2, weak a.f. coupling) Mossbauer: 2 indistinguishable Fe(II)



Oxyhemeritrin

Purple (LMCT, prob. from O_2^{2-} to Fe(III)) 1 O_2 2 Fe(III) I.s. ($S = \frac{1}{2}$, strong a.f. coupling) Resonant Raman: 848 cm⁻¹ Mossbauer: 2 different Fe(III)

Resonance Raman



Resonance (top) and non-resonance (bottom) Raman spectra of MoS_2 on silicon. The excitation at 633 nm, near an electronic transition, causes appearance of bands that are too faint to be visible with excitation at 532 nm.

Mössbauer spectroscopy (Rudolf Mössbauer, Nobel Prize for Physics in 1961)



-1.0

-0,5

0

0,5

1,0

 δ /mm s⁻¹

2,0

1,5

Ribonucleotide reductase (RNR)



Active site and metal cofactors in different classes of Ribonucleotide reductases



Radical mechanism of RNR









Hypothetical catalytic cycle of MMO



P and Q are spectroscopically characterized intermediates

Active site of an acidic phosphatase (catalyzes the hydrolysis of phosphate monoesters)



Tyr (LMCT, λ_{max} fra 510 e 550 nm), responsible for the pink-to-purple color

Catalytic cycle of an acidic phosphatase



active site: Fe(III)-Fe(II) Both high-spin

Fe–S proteins

Electron transfer process at negative potentials



Cubanoid structure



[2Fe-2S]



[4Fe-4S]

Cubanoid structure



[3Fe-4S]

[Ni–Fe]-hydrogenase: redox path



Rubredoxin from clostridium pasteurianum



Iron-sulfur units in ferredoxins

E° between –250 and –450 mV



Rieske protein from spinach chloroplasts



High Potential Iron-sulfur Proteins (HiPIP)



Model complexes



6 RSH + 4 NaHS + 4 FeCl₃ + 10 NaOR \rightarrow Na₂[Fe₄S₄(RS)₄] + 10 ROH + 12 NaCl + RSSR



Aconitase enzyme

Catalyzes the interconversion of citrate to isocitrate



Citrato

Aconitato

Isocitrato

