

BIOINORGANIC CHEMISTRY

1. Porphyrin Ring System and Metalloporphyrins

- Porphyrins are cyclic compounds with four pyrrole rings linked by methine bridges ($-\text{CH}=\text{}$).
- They form a conjugated π -electron system, imparting intense colors (Soret band).
- Central cavity binds metal ions forming metalloporphyrins (e.g., Fe^{2+} in heme, Mg^{2+} in chlorophyll).
- Metalloporphyrins serve as prosthetic groups in many biological molecules.

2. Haemoglobin and Myoglobin

- Haemoglobin: A tetrameric protein with four heme groups; each binds one O_2 molecule.
- Myoglobin: Monomeric, stores O_2 in muscles, higher affinity than haemoglobin.
- In deoxyhemoglobin/myoglobin, Fe(II) is high-spin (d^6 , $S = 2$) in a nearly octahedral field with one coordination site vacant or weakly occupied by water.
- Upon O_2 binding, Fe(II) remains formally ferrous but becomes low-spin (d^6 , $S = 0$) due to the strong-field nature of O_2 , leading to increased crystal field splitting and partial $\text{Fe(III)}-\text{O}_2^-$ character. The iron moves into the porphyrin plane, stabilizing the oxy form.

- Oxygen binding is cooperative in haemoglobin but non-cooperative in myoglobin.

3. Chlorophyll

- A magnesium porphyrin complex with a phytol tail for membrane attachment.
- Main types: Chlorophyll-a (blue-green) and Chlorophyll-b (yellow-green).
- Essential for photosynthesis – absorbs light and transfers energy to reaction centers.

4. Iron–Sulphur Proteins

- Contain Fe and S atoms arranged as $[\text{2Fe}-\text{2S}]$, $[\text{3Fe}-\text{4S}]$, or $[\text{4Fe}-\text{4S}]$ clusters.
- Act as electron carriers in redox reactions (e.g., ferredoxin, aconitase).
- Iron alternates between Fe^{2+} and Fe^{3+} oxidation states.

5. Metalloenzymes

- Enzymes containing essential metal ions at active sites for catalysis.
- Examples: Carbonic anhydrase (Zn^{2+}), Catalase (Fe^{3+}), Nitrogenase (MoFe complex).
- Metal ions stabilize enzyme structure and participate in electron transfer or substrate activation.

6. Photosynthesis (Photosystem I & II)

- Photosystem II (PSII): Contains P680 chlorophyll, oxidizes water to O₂, releases electrons.
- Photosystem I (PSI): Contains P700 chlorophyll, reduces NADP⁺ to NADPH.
- Electron transport chain connects PSII → Cyt b₆f → PSI, generating ATP via photophosphorylation.

7. Metal Storage and Transport (Fe, Cu, Zn)

- Iron: Stored as ferritin and hemosiderin; transported by transferrin.
- Copper: Stored bound to metallothionein; transported by ceruloplasmin and albumin.
- Zinc: Stored in metallothionein; acts as a cofactor in enzymes like alcohol dehydrogenase.