

**Design and Synthesis of Redox or Catalytically Active Artificial Metalloproteins
Containing Non-native Inorganic and Organometallic Complexes**

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Abstract: The design and synthesis of new proteins with novel binding and catalytic properties has been an active area of study for the past three decades. In an effort to expand the redox and catalytic activity of native proteins and to transform synthetic inorganic and organometallic complexes into environmentally benign asymmetric catalysts, we have covalently attached metal complexes, such as ferrocene and manganese salen to the active sites of cytochrome *c* peroxidase (CcP), sperm whale myoglobin (Mb) and azurin variants containing cysteine residues. The new metalloproteins were characterized by UV-Vis, CD, electrospray mass spectroscopy and cyclic voltammetry. These results, together with chemical reactivity studies, demonstrate that the encapsulation of metal complexes by CcP, Mb and azurin have led to specifically and reversibly modified enzymes with catalytic or redox activity in aqueous solution. The significance of these results regarding protein design, green chemistry and asymmetric catalysis will be discussed.