

Metalloporphycenes are attractive artificial cofactors for myoglobin

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Porphycene is a constitutional isomer of porphyrin first prepared by E. Vogel.¹ It is known that the reduced symmetry of the porphycene framework exhibits physicochemical properties that are significantly different from those of porphyrin. Furthermore, it is of great interest to study the reactivities of metalloporphycenes. Therefore, our group has focused on replacing native heme with metalloporphycenes as artificial cofactors for hemoproteins to generate new biomaterials and catalysts.

Myoglobin is a well-known simple O₂ storage protein with protoheme IX, a cofactor for the heme pocket via non-covalent interaction. The corresponding apoprotein after removal of heme will be suitable for reaction scaffolds. Therefore, our group has attempted to obtain a reconstituted protein by inserting metalloporphycenes into apomyoglobin and obtained the following results (Figure 1):²

(1) Myoglobin reconstituted with iron porphycene shows much higher O₂ affinity with opposite O₂/CO discrimination compared to native myoglobin.

(2) Iron porphycene accelerates the cyclopropanation of styrene and the dehydration of aldoximes to nitriles in the myoglobin scaffold.

(3) Manganese porphycene promotes the hydroxylation of inert alkanes via C(sp³)-H bond activation in the presence of H₂O₂.

In this presentation, I will introduce the characteristics of metalloporphycenes in myoglobin.

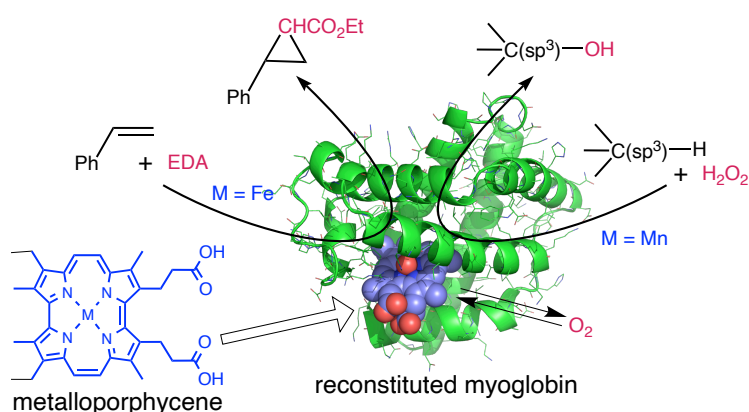


Figure 1. Reactions catalyzed by myoglobin reconstituted with metalloporphycene.

References:

- 1) Vogel, E.; Kocher, M.; Schickler, H.; Lex, J. *Angew. Chem. Int. Ed. Engl.*, **1986**, *25*, 257-259.
- 2) Oohora, K.; Onoda, A.; Hayashi, T. *Acc. Chem. Res.*, **2019**, *52*, 945-954.