

Metalloporphyrinoids as Artificial Cofactors for Preparation of Reconstituted Myoglobins

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Myoglobin is an oxygen-storage hemoprotein that generally exhibits no enzymatic activity. In contrast, apomyoglobin, obtained by removing a heme cofactor from the heme pocket, can serve as an attractive reaction scaffold because it allows artificially synthesized metalloporphyrinoids to be inserted into the apoprotein cavity. Our group has focused on generating artificial metalloproteins by replacing the native heme cofactor with a metalloporphyrinoid. Recently, our group has prepared three types of porphyrinoids; a constitutional porphyrin isomer such as porphycene, a cyclic tetrapyrrole compound lacking one meso-carbon such as corrole or corrin derivatives, and substituent-modified protoporphyrins (Figure 1). After the metalation of the porphyrinoids, myoglobins reconstituted with each complex were found to function as an artificial enzyme or serve as a model for unclear metalloenzymes.¹ For example, myoglobin reconstituted by manganese porphycene promoted the hydroxylation of inert alkane species to give the corresponding alcohol as a product.² Iron porphyrin with CF₃ groups at peripheral positions works as a catalyst for the cyclopropanation of olefins with ethyl diazoacetate in the myoglobin scaffold.³ Furthermore, it is found that cobalt corrin derivatives are an excellent cofactor model for cobalamin in the myoglobin heme pocket.⁴ This presentation describes several myoglobins reconstituted with metalloporphyrinoids, as well as their physicochemical properties and catalytic activities.

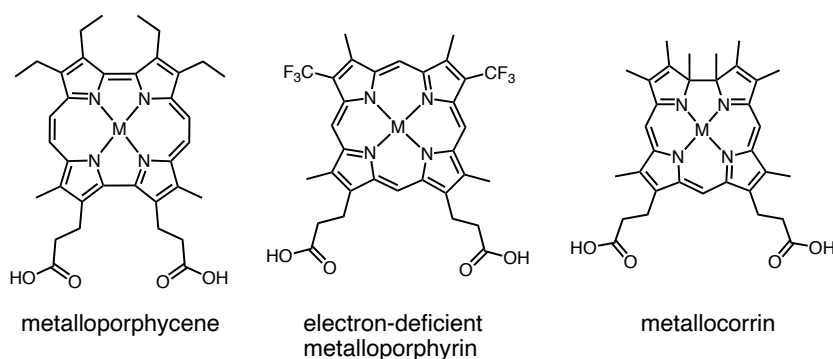


Figure 1. Three types of metalloporphyrinoids as a myoglobin cofactor

This work was supported by JSPS KAKENHI (particularly, 25H00887 and 22K21348).

References

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