For sustainable chemistry, protein is one of the promising materials due to the fine-tuned functions accompanied by the sophisticated structures. In this context, the present work has demonstrated the chemical approach of modification of hemoproteins toward biomaterials and artificial metalloenzymes. To replicate natural protein assemblies, heme–heme pocket interaction is an appropriate driving force to create new-type of supramolecular assembly. The replacement of the heme (porphyrin iron complex) cofactor with artificial metal complex is a significantly useful method to modify the reactivities. Especially, this applicant has achieved the following three results using "interaction between metal porphyrinoid and heme pocket in hemoprotein".

i) Supramolecular assembling system of hemoproteins (*J. Am. Chem. Soc.* **2018**, *Chem. Commun*. In press, *Chem. Lett.* In press)

In biological systems, protein assemblies with sophisticated structures achieve unique functions. To replicate such system by chemical approach, we have demonstrated a series of the supramolecular assembling systems of hemoprotein driven by heme–heme pocket interactions. Particularly, the optimization of the monomer unit provides the well-defined helical fiber formed by protein assembly via heme–heme pocket interactions and induced hydrogen bonding network at protein interface in recent our work. The helical protein fiber shows unique cellular uptake behavior, which clearly expresses multi valent effect of cell-penetrating peptide tags efficiently generated by well-organized structure. In near future, these systems will contribute to the development of biomaterials toward biomedical applications.

ii) Catalytic hydroxylation of C–H bonds using myoglobin reconstituted with manganese porphycene (*J. Am. Chem. Soc.* **2017**, *J. Am. Chem. Soc.* **2013**)

Myoglobin is a well-known hemoprotein for oxygen storage, whereas no catalytic activity toward C–H bond hydroxylation is reported in contrast to native hemoenzymes such as cytochrome P450. Recently, the applicant found that manganese porphycene, an artificial metalloporphyrinoid, serves as an active site toward catalytic C–H bond hydroxylation in the reconstituted myoglobin. The reconstituted protein is capable of hydroxylation of ethylbenzene, toluene and cyclohexane using hydrogen peroxide as a terminal oxidant under mild conditions at pH 8.5 and 25ºC. Interestingly, the manganese(V)-*oxo* species is spectroscopically detectable as an active species in this system. Detailed mechanistic investigation suggests the catalytic hydroxylation by the rate-determining H atom abstraction and following OH-rebound, which is similar to the mechanism found in cytochrome P450.

iii) Abiological cyclopropanation reaction by myoglobin reconstituted with iron porphycene (*J. Am. Chem. Soc.* **2017**)

Cyclopropanation of styrene by ethyl diazoacetate as a carbene source is one of the most interesting abiological reactions catalyzed by hemoprotein. However, the active metallocarbene has not been studied well. Using the iron porphycene as an artificial cofactor, the applicant achieves the efficient formation and spectroscopic characterization of the active metallocarbene. The overall catalysis is also 600-fold accelerated by cofactor replacement compared with native myoglobin. The theoretical investigation supported the rapid metallocarbene formation, indicating the importance of stronger ligand field effect of porphycene to stabilize the triplet of resting state compared with porphyrin.