Construction of Heme Protein HasA Capturing Artificial Metal Complexes for Novel Biocatalysts

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meso-Tetraphenylporphyrin (TPP) is a simple porphyrin that can be synthesized by acid-catalyzed condensation of pyrrole with benzaldehyde in good yield, and its derivatives can be easily prepared by using the corresponding aldehydes. Therefore, TPP and its derivatives have been widely used as multiporphyrin architectures, photosensitizers and catalysts based on their photochemical and redox properties. However, even simple TPP has never been incorporated into native proteins because of the four bulky and hydrophobic phenyl groups on its meso positions. It was necessary to find a protein with a space that could accommodate bulky TPP for using unique properties of TPP as prosthetic groups of proteins. Our group focused on heme acquisition protein HasA secreted by *Pseudomonas aeruginosa*. The heme-binding site of HasA is highly exposed to solvent, thereby the moiety of the captured heme can be seen from outside of HasA in the crystal structure of HasA with heme. This notable heme-binding feature allows the accommodation of various artificial metal complexes which are totally different structures from heme.[1-4]

In this study, we constructed the artificial metalloproteins capturing FeTPP by using a HasA. We also succeeded in the X-ray crystal structure analysis of HasA capturing FeTPP (Fig. 1) and evaluated the structural changes induced by FeTPP. To the best of our knowledge, this is the first example of a natural protein that stably binds FeTPP. Furthermore, we found that HasAs containing FeTPP can be used as biocatalysts by tailoring the active site through mutagenesis for the accommodation of substrates.

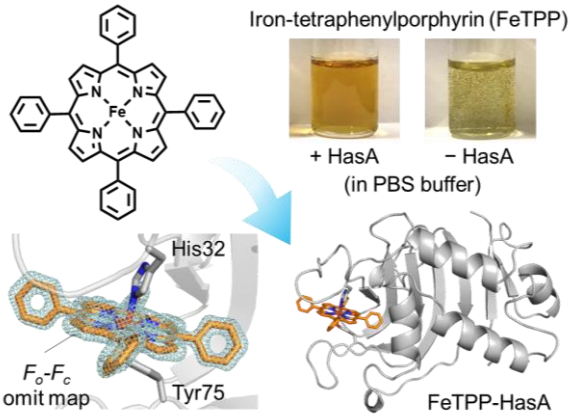

Fig. 1 Crystal structure of FeTPP-HasA

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