Takashi HAYASHI, Professor

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Education

Ph. D. (March, 1990), M. Eng. (March, 1987), B. Eng. (March, 1985): Kyoto University

Academic Carrier

1990 (April) – 1997 (June): Assistant Professor, Department of Synthetic Chemistry and Biological Chemistry, Faculty of Engineering, Kyoto University

1995 (August) – 1996 (September): Visiting Scientist, Department of Chemistry, The Scripps Research Institute

1977 (July) – 2005 (March): Associate Professor, Department of Chemistry and Biochemistry, Kyushu University

2000 (October) – 2003 (September): Project Leader on Precursory Research for Embryonic Science and Technology in JST (PREST)

2005 (April) – : Professor, Department of Applied Chemistry, Faculty of Engineering, Osaka University

2005 (April) – 2007 (March): Visiting Professor, Institute of Molecular Science

2010: Visiting Professor, Department of Chemistry, University of Strasbourg

Awards and Honors

Kaneka Corporation Award in Synthetic Organic Chemistry (1992), Inoue Research Award for Young Scientists (1992), The Progress Award on Synthetic Organic Chemistry, Japan (2000), 1st Young Investigator Award in Porphyrin Chemistry (2000), 2001 Kyushu University President Award (2002), 7th Research Promoted Award on Enzyme Application supported by Amano Enzyme Inc. (2006), Bull. Chem. Soc. Jpn. Award (2008), The Chemical Society of Japan (CSJ) Award for Creative Work (2010), The Osaka University Award for Research and Education (2011).

Total Publications

approximately 100 original papers and 6 book chapters

Research Interests

1) Synthesis, Structure and Reactivity of Porphyrins and Metalloporphyrins

- 2) Hemoproteins Reconstituted with Non-natural Prosthetic Groups
- 3) Modification of Metalloproteins
- 4) Elucidation of Molecular Mechanism of Hemoproteins
- 5) Supramolecular Self-Assembly of Proteins
- 6) Construction of Artificial Metalloenzyme

Modification and Functionalization of Hemoproteins

Takashi Hayashi

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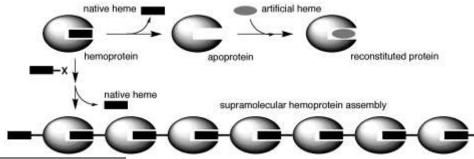
A series of hemoproteins has one or several heme prosthetic groups within their interiors. It is well-known that these proteins perform a variety of functions in biological systems, such as dioxygen storage and transfer, catalysis, electron-transfer, and gas sensing, due to the versatile reactivity of heme, iron porphyrin. Particularly, the typical prosthetic group is protoheme IX which is bound in the protein pocket via non-covalent and coordination interactions. Thus, it is possible to replace native heme with a modified metal complex as shown in the following Figure. Our group has recently focused on the reconstitution of hemoproteins with an artificial prosthetic group to obtain a functionalized protein.¹ In this presentation, our three topics will be presented.

(i) Introduction of some functional groups into the termini of the heme-propionate side chains to construct an artificial interface on the protein surface: For example, the interface acts as a substrate-binding site near the heme pocket in myoglobin, and the peroxidase activity of the reconstituted myoglobin was close to that of horseradish peroxidase (HRP).²

(ii) Replacement of native heme with an artificial metalloporphyrinoid: Myoglobin and HRP reconstituted with iron porphycene, a constitutional isomer of heme, showed dramatically enhanced dioxygen affinity and peroxidase activity, respectively.³

(iii) Supramolecular hemoprotein self-assembly by interprotein interaction between an external heme and heme pocket to create new bionanomaterials: Heme moiety was introduced onto the hemoprotein surface via covalent linkage and the following removal of native heme from the heme pocket provided a successive hemoprotein array with the length of 200–800 nm including 50–200 proteins.⁴ Furthermore, the hemoprotein layer on a gold surface and gold nanoparticle self-assembly are found to be available by use of the strategy of the hemoprotein assembly.⁵

These methods will serve as a new way to prepare a functional device using metalloprotein materials.



(1) Hayashi, T. In *Handbook of Porphyrin Science;* Kadish, K. M.; Smith, K. M.; Guilard, R. Eds.; World Scientific Publishing: Singapore, 2010; Vol. 5, pp 1–69.

(2) Matsuo, T.; Fukumoto, K.; Watanabe, T.; Hayashi, T. Chem. Asian, J. 2011, 6, 2491-2499.

(3) (a) Matsuo, T.; Murata, D.; Hisaeda, Y.; Hori, H. Hayashi, T. J. Am. Chem. Soc. 2007, 129, 12906–12907, (b) Matsuo,

T.; Hayashi, A.; Abe. M.; Matsuda, T.; Hisaeda, Y.; Hayashi, T. J. Am. Chem. Soc. 2009, 131, 15124–15125.

(4) (a) Kitagishi, H.; Oohora, K.; Yamaguchi, H.; Sato, H.; Matsuo, T.; Harada, A.; Hayashi, T. J. Am. Chem. Soc. 2007, 129, 10326–10327. (b) Kitagishi, H.; Kakikura, Y.; Yamaguchi, H.; Oohora, K.; Harada, A.; Hayashi, T. Angew. Chem. Int. Ed. 2009, 48, 1271–1274. (c) Oohora, K.; Onoda, A.; Kitagishi, H.; Harada, A.; Hayashi, T. Chem. Sci. 2011, 2, 1033–1038. (5) (a) Onoda, A.; Ueya, Y.; Sakamoto, T.; Uematsu, T.; Hayashi, T. Chem. Commun. 2010, 46, 9107–9109, (b) Onoda, A.; Kakikura, Y.; Uematsu, T.; Hayashi, T. Angew. Chem. Int. Ed. in press.