Unusual Dioxygen Affinity of Myoglobin Reconstituted with an Artificially Created Iron Complex

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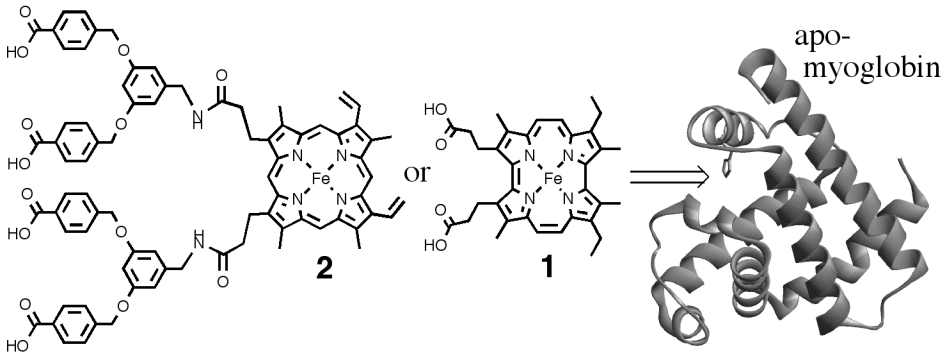
Functionalization of hemoproteins is one of the attractive subjects for creating a new biomaterial. Recently, we have prepared various artificial prosthetic groups and inserted them into apomyoglobin to obtain reconstituted myoglobins. For example, a porphycene iron complex **1** as shown below is a unique prosthetic group. Compared to native myoglobin, the reconstituted myoglobin with **1** is clearly stable against acid denaturation, indicating the Fe–His93 bond strength is strong. The O_2 affinity of the ferrous **1** is higher by 2600-fold than that of the wild-type myoglobin, mainly due to the decrease in the O_2 dissociation rate. In addition, the *M*' value, which is a ratio of CO/O_2 affinity, is less than 1. On the other hand, a reconstituted myoglobin having **2** with a hydrophobic domain at the terminal of the two heme-propionate side chains shows unusual CO/O_2 discrimination. The substantial ligand selectivity for the reconstituted myoglobin remarkably increases in favor of O_2 over CO with the *M*' value of 0.88, indicating that the modification of heme-propionate side chains only perturbed CO affinity. These data suggest that the incorporation of an artificially created heme will lead to an effective regulation of a ligand binding. In this presentation, we summarize our recent results of ligand binding studies using the reconstituted myoglobins.



1) T. Matsuo, T, Hayashi *et al. J. Am. Chem. Soc.* **2004**, *126*, 16007–16017.
2) H. Sato, T. Hayashi *et al. J. Am. Chem. Soc.* **2005**, *127*, 56–57.