Construction of Hemoprotein Dimers Using Rigid Porphyrin Oligomers Toward Artificial Hemoprotein Assemblies

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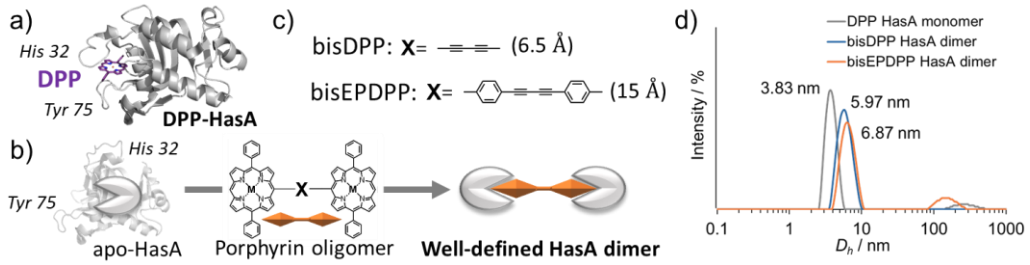
Hemoproteins are among the most versatile metalloproteins, and heme substitution is a widely utilized method to introduce additional functions into hemoproteins for constructing artificial hemoprotein assemblies.[1] The heme acquisition protein HasA, secreted by gram-negative bacteria, can capture various metal complexes different from heme, such as diphenylporphyrins (DPPs)[2] (Fig. a) and tetraphenylporphyrins (TPPs).[3] Using this unique property of HasA, we recently succeeded in constructing a metal ion-driven HasA dimer by incorporating TPP with an additional metal coordination site into HasA.[4] By combining the synthetic designability of porphyrins with the high acceptability of HasA against synthetic porphyrins, HasA represents a promising platform for constructing well-defined artificial hemoprotein assemblies.

In this study, we attempted to construct well-defined HasA dimers as an initial step toward constructing HasA assemblies based on rationally designed porphyrin derivatives (Fig. b). To enhance the stability of porphyrin-HasA complexes compared to TPP, we selected DPP as the base structure and synthesized two types of DPP dimers with different lengths of rigid linkers (Fig. c). After optimizing the reconstitution conditions, we successfully reconstituted HasA with these synthesized dimers and obtained the desired HasA dimers. The resulting HasA dimers exhibited red-shifted UV-vis spectra and larger hydrodynamic diameters (D_h) (Fig. d) compared to the corresponding monomer. These results indicate that the properties of HasA dimers accurately reflect the features of the porphyrin dimers incorporated into them. This finding suggests that the characteristics of HasA dimers can be precisely controlled by rationally designing the porphyrin dimers. We are currently exploring the construction of HasA dimers using other porphyrin oligomers.



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