

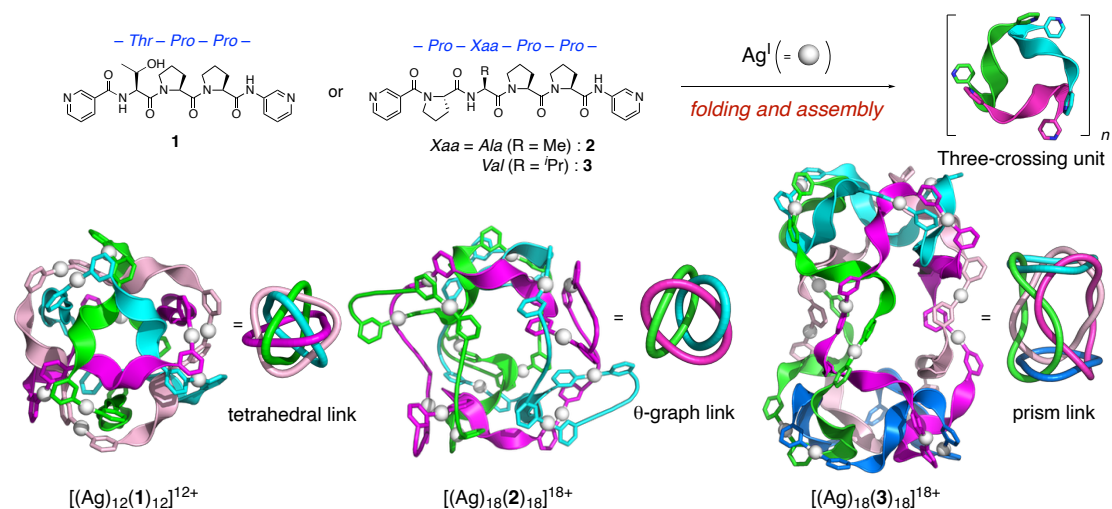
## Metal-induced folding and assembly through three-crossing peptidic units

(<sup>1</sup>Grad. School of Engineering, The University of Tokyo, <sup>2</sup>JST PRESTO, <sup>3</sup>Institute for Molecular Science) ○Ami Saito<sup>1</sup>; Tomohisa Sawada<sup>1,2</sup>; Makoto Fujita<sup>1,3</sup>

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In the field of molecular topologies, it has still been challenging to synthesize a molecular *polyhedral link*, which is a framework of multiple macrocycles interlocking in a polyhedral manner. In this work, we constructed such molecular polyhedral links by using a peptide-based three-crossing unit. During the course of studies on the folding-and-assembly method,<sup>[1]</sup> which utilizes concomitant processes of short peptides folding and their metal-directed self-assembly, we found the combination of Ag(I) ions and a bis-pyridyl appended peptide ligand of the Thr-Pro-Pro sequence (**1**) gave a *tetrahedral link* framework based on a three-crossing unit. Moreover, we developed a series of polyhedral links by extending the peptide sequence.

First, complexation of ligand **1** and Ag(I) ions gave a self-assembled  $[\text{Ag}_{12}(\mathbf{1})_{12}]^{12+}$  structure. Crystallographic study revealed the formation of a *tetrahedral link* framework, where four units of the three-crossing motif (**1**)<sub>3</sub> were self-assembled in *T* symmetry.<sup>[2]</sup> We then designed the tetrapeptide sequences, Pro-Ala-Pro-Pro (**2**) and Pro-Val-Pro-Pro (**3**). Complexation of Ag(I) ions and ligands **2** and **3** gave the  $[\text{Ag}_{18}(\mathbf{2})_{18}]^{18+}$  and  $[\text{Ag}_{18}(\mathbf{3})_{18}]^{18+}$  complexes, respectively. Crystallographic studies revealed the formation of a *θ-graph link* that includes two units of three-crossing motif (**2**)<sub>3</sub> and a *triangular prism link* that consists of six units of three-crossing motif (**3**)<sub>3</sub>, respectively. Thus, we succeeded in construction of a series of polyhedral links by extending the peptide sequence via the three-crossing unit design.



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