

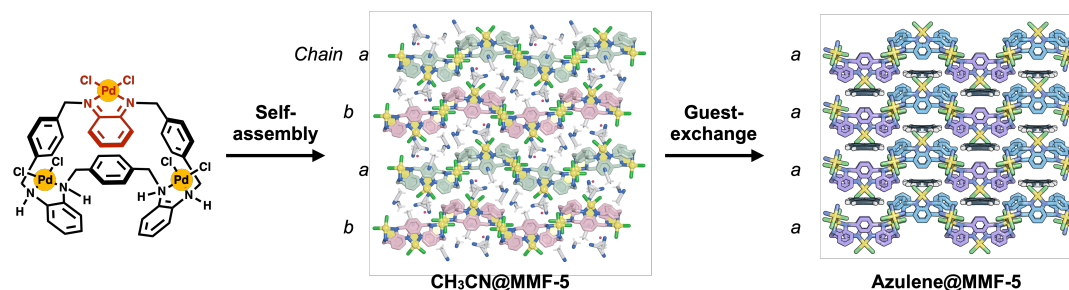
Construction of a dynamic porous crystal, metal-macrocycle framework-5 (MMF-5), formed by zigzag packing of oxidized metallo-macrocycles

(¹Graduate School of Science, The University of Tokyo) ○ Wei He,¹ Shohei Tashiro,¹ Mitsuhiro Shionoya¹

Keywords: Self-assembly; Oxidation; Pd complex; Molecular recognition; Macrocylic compound

Dynamic porous crystals, which can adjust their structure and function in response to external stimuli, have been of great interest in the fields of catalysis, storage, and separation. The assembly mode of the building blocks plays an important role in the formation of dynamic porous crystals. We have previously reported porous metal-macrocycle frameworks (MMF-1, MMF-2, and MMF-3) formed by self-assembly of Pd₃-macrocycles.^{1,2} Macrocycle-based molecular binding sites in MMFs enable multipoint molecular recognition *via* non-covalent interactions in the confined space of MMF. The development of dynamic functions based on self-assembled macrocyclic compounds is the next major challenge.

In this study, we found that a new porous MMF-5 with excellent guest recognition ability can be crystallized by the partial oxidation of the metallo-macrocylic building blocks. In MMF-5, one *o*-phenylenediamine-Pd(II) moiety of each Pd₃-macrocycle was oxidized to the diimine-Pd(II) structure. This partially oxidized structure was determined by single-crystal XRD analysis and spectroscopic studies including UV-vis and IR analysis. In the crystal structure, the partially oxidized Pd₃-macrocycles were packed in a zigzag pattern, forming one-dimensional chains by Pd^{II}-Pd^{II} interactions and multipoint hydrogen bonding. These highly ordered chains were further assembled into a two-dimensional network and crystalline MMF-5. Furthermore, the unique packing mode of the oxidized Pd₃-macrocycles resulted in the dynamic nature of MMF-5. Single-crystal XRD analysis revealed that the porous crystal structure of MMF-5 is dynamically changed by sliding zigzag packing structure caused by the single-crystal-to-single-crystal guest exchange.



1. S. Tashiro, R. Kubota, M. Shionoya, *J. Am. Chem. Soc.* **2012**, 134, 2461.
2. R. Kubota, S. Tashiro, M. Shionoya, *Chem. Sci.* **2016**, 7, 2217.