Structural control of a porous metal–macrocycle framework based on molecular adsorption to a local allosteric site

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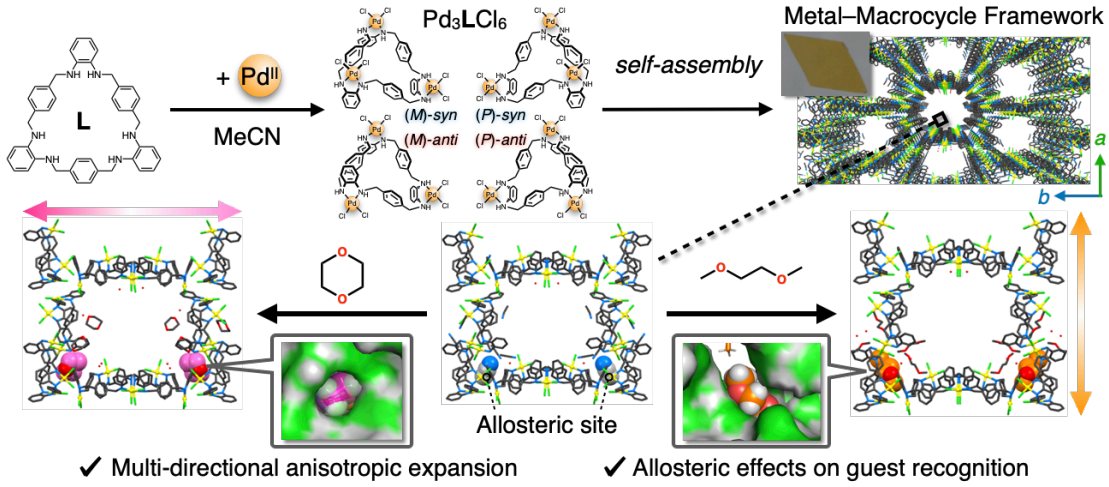
Dynamic conformational changes in biomacromolecules driven by molecular recognition at an allosteric site are essential for the precise regulation of their activity, and it is challenging to artificially design such elaborate systems. Previously, our group has developed a Pd^{II}-macrocycles-based porous molecular crystal, metal–macrocycle framework (MMF). It has five different guest recognition sites on one-dimensional nano-channels and site-selectively adsorbs various molecules. [1]

In this study, we found a multi-directional anisotropic transformation of the channel structure by introducing small effector molecules. For example, expansion along the *a*-axis was induced in 1,2-dimethoxyethane, whereas the expansion was observed along *b*-axis in 1,4-dioxane. Single-crystal XRD analysis revealed that one of the guest recognition pockets of the Pd^{II}-macrocycle was specifically deformed depending on the effector contained. Therefore, it was shown that this pocket could function as an allosteric site to determine the entire crystal structure, where molecular encapsulation led to the rearrangement of Pd^{II}-macrocycle inducing the cell transformation. As a result, the crystal structure can be reversibly controlled in various directions depending on the effector molecules. In addition, we demonstrated allosteric effects of conversion on the guest adsorption to other free binding pockets. The guest recognition ability can be regulated allosterically based on the dynamic structural changes.



1) S. Tashiro, R. Kubota, M. Shionoya, *J. Am. Chem. Soc.* **2012**, *134*, 2461.

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