Pore structure transformation and shape memory effect of a porous metal–macrocycle framework based on local adsorption of effector molecules

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The higher-order structures of allosteric proteins precisely regulate their activity by specifically recognizing effector molecules at local binding sites. The allosteric regulation of artificial supramolecular structures based on the specific recognition of effector molecules is a promising approach for the development of bio-inspired functional materials.

Our group has previously reported porous supramolecular crystals, metal–macrocycle frameworks (MMFs), constructed by self-assembly of Pd_3-macrocycles[1] (Figure a). MMFs have a low-symmetric one-dimensional channel with multiple recognition sites that can selectively adsorb guest molecules. Recently, we found that when effector molecules are adsorbed into specific molecular recognition pockets of MMF channels, the crystal structure of the entire MMF exhibits reversible anisotropic extension. Single-crystal XRD analysis revealed that the non-covalent interactions among Pd_3-macrocycles are specifically reformed depending on the type of effectors adsorbed. As a result, the crystal structure of MMF can be controlled in various ways depending on the type and binding mode of the effector molecules. Furthermore, it was found that the extended structure is maintained in a metastable state by the dynamic binding of the newly designed effector molecules (Figure b). This structure was converted to its original state by releasing effector molecules through heat treatment, indicating that MMF crystals have a shape-memory function.

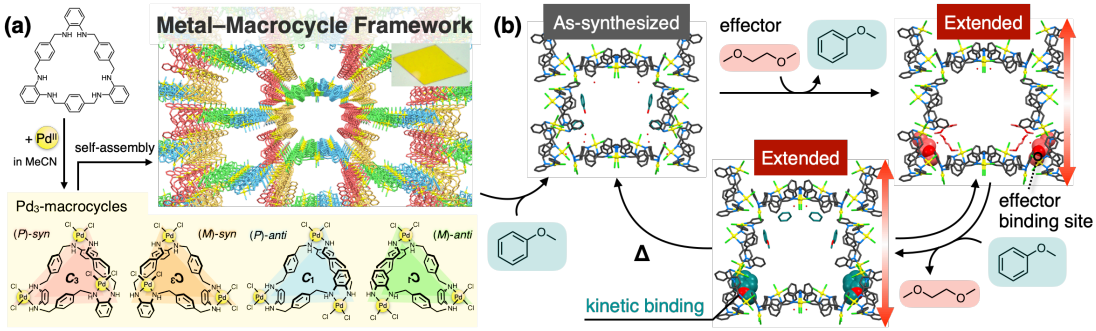

Figure (a) Construction of MMF crystals, **(b)** Pore structure transformation and shape-memory effect of MMF

[1] (a) S. Tashiro, R. Kubota, M. Shionoya, *J. Am. Chem. Soc.* **2012**, *134*, 2461. (b) S. Tashiro, M. Shionoya, *Acc. Chem. Res.* **2020**, *53*, 632.