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Direct Crystallographic Observation of Chemical Transformations within a Self-Assembled Cages. Makoto Fujita, Dept. of Applied Chemistry, School of Engineering, The Univ. of Tokyo, and CREST, Japan Science and Technology Agency (JST), 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.

Cavity-directed chemical transformations represent one of the most important features of three-dimensional hosts, but yet have been less explored in previous synthetic receptors. We are developing such functions with the large cavity of the self-assembled cages, particularly an M_6L_4 -type cage complex. The photodimerization of olefins in this cage is featured, for example, by remarkable rate enhancement ($>10^2$ times), perfect regio- and stereo-selection, and high pairwise selection (when two different olefins are used) giving only a cross [2+2] adduct. In this paper, chemical reactions are carried out in a single crystalline state of the cage-substrate complex. Despite considerable change in the structures of the substrates, the cage framework is sufficiently robust enough to allow the direct crystallographic observation of the chemical reactions without losing the single crystallinity. The generation and trapping of an extremely labile unsaturated metal complex as well as solution-like behavior of an olefin in the [2+2] photoaddition in crystalline cage will be discussed.