In Situ Crystallographic Observation of Highly Selective Organic Reactions in Supramolecules

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Reactive intermediates in organic reactions have been intensively studied with spectroscopic methods. Recent development of theoretical calculation for vibrational analysis significantly promoted structural studies of reactive unusual molecules in inert matrices. However, crystallographic analysis has been hardly applied to direct observation of molecular structures of reactive intermediates, although it has been widely used for structural characterization of stable compounds. In this talk, in situ observation study of unstable species by X-ray crystallography will be introduced. A principal method we use is cryo-trapping rather than time-resolved techniques, to freeze photo-induced short-lived intermediates at low temperatures. Note that, the latter can be used only for completely reversible reaction systems such as photo-excited state, whereas the former can be applied to irreversible ones. Moreover, we would like to introduce *a supramolecular approach* via a self-assembled coordination cage for crystallographic in situ observation to overcome pitfalls of conventional in situ techniques. The salient features of the supramolecular approach are that one can suppress inevitable deterioration of single crystallinity induced by photo-irradiation and investigate even non-crystalline molecules as long as they can be encapsulated in a host where the host should be readily crystallized. Here we will introduce highly selective photoreactions in a nano-space of a giant coordination cage in crystalline state.