

Sequential Synthesis of Multinuclear Metal Clusters by Using Multivacant Lacunary Polyoxometalates and Precise Control of Chemical/Physical Properties

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Numerous types of multinuclear metal clusters within organic and inorganic ligands are known to exhibit unique chemical and physical properties that are largely dependent on the types, nuclearities, combinations, and coordination geometries of the constituent metal cations. Therefore, it is extremely important for developing novel molecular materials that possess excellent catalytic, redox, luminescent, and magnetic properties to precisely synthesize multinuclear metal clusters as designed at the atomic level and to control their properties by slightly changing the structures and coordination geometries of their metal cations. However, these multinuclear metal clusters have been synthesized mainly by the empirical one-step reactions of metal sources with ligands, thus making it difficult to predict the structures of the final products and to control the structures precisely. Moreover, the synthesis of multinuclear metal clusters of different types and nuclearities is still quite difficult even by using highly designed multidentate organic or inorganic ligands.

Through the work at the University of Tokyo, several new organic-solvent-soluble multivacant lacunary polyoxometalates (POMs), which act as rigid multidentate inorganic ligands for constructing multinuclear metal clusters, have been successfully developed. By introducing metal cations into vacant sites of POM ligands, various types of hetero-multinuclear metal clusters could be selectively synthesized (Figure 1). This sequential synthesis method proved to be an effective method for constructing multinuclear metal clusters with many cation types (up to 4 types per molecule and over 13 types at one coordination site) and nuclearities (up to 24 metals) at the atomic level. By selecting the types of atoms as designed, these clusters showed unique magnetic properties, such as single-molecule magnet (SMM) properties, large spin ground states, and unusual intermolecular ferromagnetic interactions. In addition, at University of Glasgow, automation of

this sequential synthesis method using robot platform was successfully performed, leading to the discovery of new SMMs with the highest energy barrier among the previously reported transition metal-substituted POMs. Combination of unique redox properties of POMs with metal complexes, which can activate hydrogen, (at Kyushu University from April) will also be introduced at the presentation.

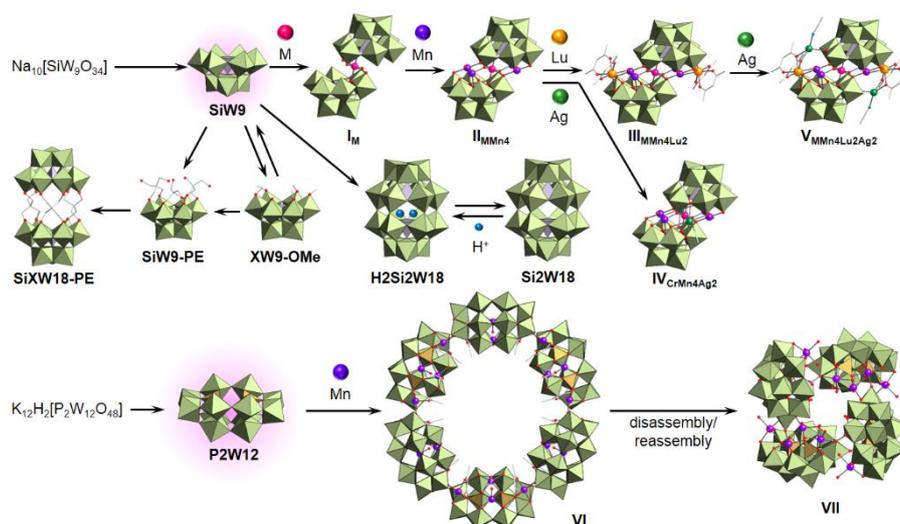


Figure 1. Schematics of sequential synthesis of multinuclear metal clusters within POMs.