Over the last decade, crystal flask that converts one chemical species to another in single-crystal-to-single-crystal (SCSC) manner has attracted much attention in crystal engineering. An important key for the construction of crystal flask is a porous space which can induce a chemical from outside of a crystal. To design such a porous space, our group has intensively studied the metallocigan approach in which a pre-prepared homometallic complex with coordination donor sites is reacted stepwise with secondary metal ions. We established the construction of a variety of metalloarchitectures by the metallocigan approach with using thiolato groups derived from amino acids and phosphine ligands. Recently, our group has successfully prepared a microporous material of a polyanion polyanion in which all ions have the ability to accommodate chemical species in crystal. Interestingly, 1CdNa has large interstices connected by 3D channels which allow the easy incorporation and accommodation of guest molecules. Therefore, it was found that 1CdNa underwent the stepwise SCSC transmetallation reactions to form AuI CuI metalloge (1Cu). Furthermore, we found that the crystals of 1Cu have the ability to accommodate MoO42− ions (2Mo1) and condense them to form Mo7O246− (2Mo7) and β-Mo8O264− (2Mo8) by the addition of protons in the solid state. These results show the availability of the large crystal interstices in 1Cu as crystal flask, which serves as a reaction field for accommodated chemical species in crystal. Such a crystal flask reaction of polyoxomolybdate will give an important insight for not only material science but also biosynthesis in Mo-storage protein (MoSto) which contains Mo8, Mo5-7 and Mo3 clusters. The detail will be discussed in the presentation.

Figure 1. Synthetic route of 1CdNa, 1Cu, 2Mo1, 2Mo7, and 2Mo8.


Keywords: Metallosupramolecules; Polyoxometalate Crystal Flask

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