

Design of Inner Space Modified Hollow-type Polyoxometalate {Mo₁₃₂}

(Graduate School of Environmental Science, Hokkaido University) ○ Chinatsu Murata, Yukatsu Shichibu, Katsuaki Konishi

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Hollow-type polyoxometalate {Mo₁₃₂O₃₇₂(H₂O)₇₂(L)₃₀}ⁿ⁻ (L = AcO⁻, SO₄²⁻ etc.; denoted by {Mo₁₃₂-L}) is a porous spherical cluster. The cluster has a molybdenum-oxide based framework, and its ligands (L) are coordinated to the inner surface of the {Mo₁₃₂-L}. In addition, guest molecules can be encapsulated through pores on the surface. However, modification of the inner environment, which leads to the tuning of selectivity for guest molecules, had not been explored. In this work, we examined the structure and inclusion behavior of a trifluoro acetate-coordinated molybdenum cluster {Mo₁₃₂-TFA}.

The cluster was obtained via ligand exchange reaction of {Mo₁₃₂-OAc} with sodium trifluoroacetate in water (Fig.1). Single crystal X-ray diffraction analysis of {Mo₁₃₂-TFA} revealed that it has a spherical structure in which CF₃ groups are introduced on the inner wall. Retention of the spherical framework after the reaction was confirmed by NMR, FT-IR and UV-Vis spectra. Next, the effect of the ligand replacement of {Mo₁₃₂-L} on the encapsulation behavior of organic molecules was investigated. From ¹H- and ¹⁹F-NMR data, we found that the organic molecules were more efficiently encapsulated into {Mo₁₃₂-TFA} than {Mo₁₃₂-OAc}. Thus, the affinity between guest molecules and host framework was enhanced through the inner surface modification.

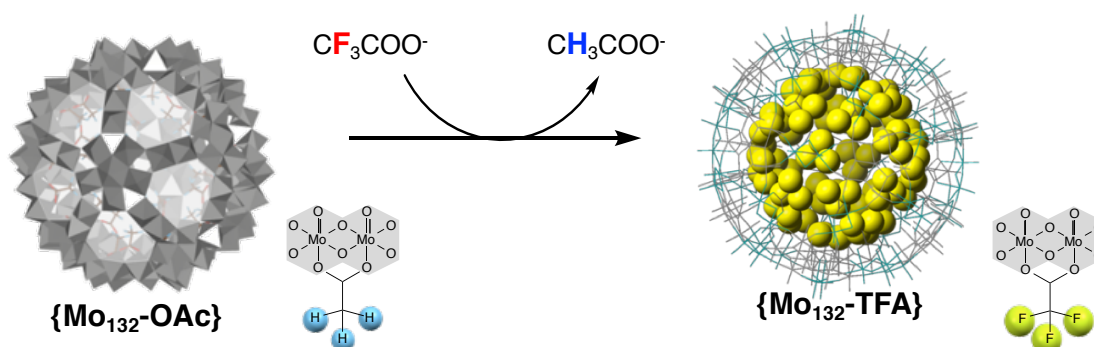


Fig. 1 Synthesis of {Mo₁₃₂-TFA} via ligand exchange reaction of {Mo₁₃₂-OAc}.

1) A. Müller *et al.*, *Chem. Soc. Rev.* **2012**, 41, 7431.