

Guest Encapsulation Behavior of Covered Fluorine-modified Hollow-type Metal Oxide Cluster $\{\text{Mo}_{132}\}$

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Hollow-type metal oxide cluster $\{\text{Mo}_{132}\text{O}_{372}(\text{H}_2\text{O})_{72}(\text{L})_{30}\}^{n-}$ ($\text{L} = \text{AcO}^-$, SO_4^{2-} , etc.; denoted by $\{\text{Mo}_{132}\text{-L}\}$) has a porous spherical structure^[1]. It has a molybdenum-oxide based framework, and ligands (L) are coordinated to the inside. In addition, guest molecules can be encapsulated through pores on the surface^[2]. However, modification of the inner environment, leading to the tuning of selectivity for guest molecules, had not been established. In this work, we examined the structure and inclusion behavior of a trifluoroacetate (TFA) modified cluster $\{\text{Mo}_{132}\text{-TFA}\}$, and the behavior was compared to that of $\{\text{Mo}_{132}\text{-OAc}\}$.

$\{\text{Mo}_{132}\text{-TFA}\}$ was obtained via ligand exchange reaction of $\{\text{Mo}_{132}\text{-OAc}\}$ with TFA in water. Single crystal X-ray diffraction revealed that it had a spherical structure in which CF_3 groups were introduced on the inner surface. Retention of the spherical structure after the reaction was confirmed by NMR, FT-IR and UV-Vis spectra. The inner environment of $\{\text{Mo}_{132}\text{-TFA}\}$ was then investigated from the encapsulation behavior of cyclic organic molecules. Encapsulations of these molecules into two types of $\{\text{Mo}_{132}\}$ hosts were shown by NMR analyses, and the number of included guest molecules were determined from quantitative NMR. As for five-membered rings, each of them was basically more efficiently encapsulated into $\{\text{Mo}_{132}\text{-TFA}\}$ than $\{\text{Mo}_{132}\text{-OAc}\}$ (Fig. 1).

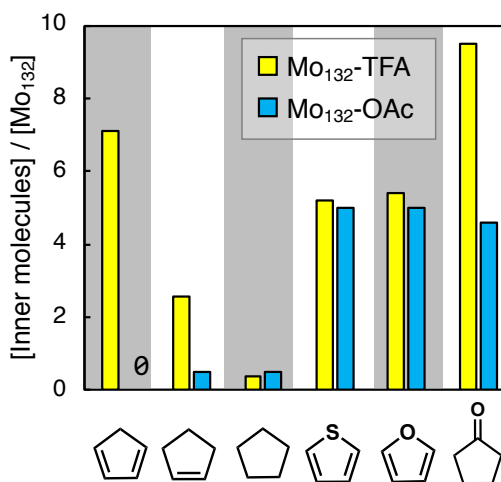


Fig. 1 Inclusion ability of $\{\text{Mo}_{132}\}$ for five-membered rings.

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