Investigation of synthesis of thiol-protected Au clusters using dendrimers

([1]*Tokyo Tech., Lab. Chem. Life Sci.*, [2]*JST-ERATO*, [3]*JST-PRESTO*) ○Hisanori Muramatsu,[1] Tetsuya Kambe,[1,2] Takamasa Tsukamoto,[1,2,3] Takane Imaoka,[1,2] Kimihisa Yamamoto[1]

Keywords: *Cluster, Au, Dendrimer, Thiol protected cluster*

Metal clusters are generally smaller than nanoparticles and consist of a few to several dozen metal atoms. Since the liquid-phase synthesis of thiol-protected Au clusters was reported by Brust and Schiffrin,[1] various Au clusters have been reported. However, synthesizing these Au clusters and hetero-metal Au clusters requires a high-yield method at low-temperature,[2] synthesis method using an etching reaction,[3] and a synthesis method using metal exchange for different metals, all of which require time. On the other hand, there is a liquid-phase synthesis method for metal clusters that use dendrimers as templates. In this method, elements to be formed clusters can be collected in dendrimers in advance, allowing direct synthesis. The 4th-generation phenylazomethine dendrimer (TPM G4) developed in our laboratory has been reported to be used for 2-5 kinds of metal salts assembly and cluster synthesis.[4] The synthesis using the TPM G4 has also been reported. Cluster synthesis of Al_{13}^- in the liquid phase, which has been synthesized in the gas phase, has been discovered so far [5]. In this study, we discuss further extensions of the synthesis of thiol-protected Au clusters using dendrimers.

$AuCl_3$ was coordinated to the dendrimer (TPM G4). The $Au_{25}PET_{18}$ cluster was synthesized by addition of $NaBH_4$ and thiol ligands to the solution of dendrimer metal complexes at the same time, to conduct reduction and thiol coordination. The synthesis of the $Au_{25}PET_{18}$ cluster was confirmed by MADLI-TOF-MS (Figure 1a). We will report on the extended results of the new synthesis of thiol-protected Au clusters achieved with $Au_{25}PET_{18}$ (Figure 1b).

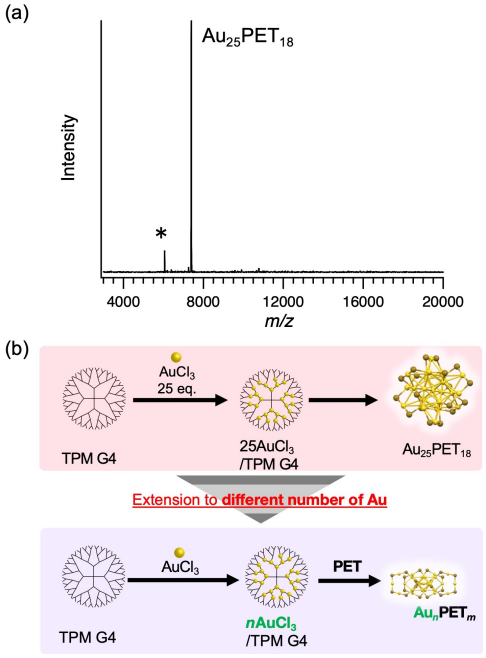

Figure 1. (a) MALDI-TOF-MS spectrum of the sample obtained after synthesis. * is $[Au_{21}PET_{14}]^+$ of the fragment of $Au_{25}SR_{18}$.[6] (b) Schematic illustration of the concept of this study.

1) Brust, M.; Schiffrin, D. J.; *et al.*, *J. Chem. Soc. Chem. Commun.*, **1994**, *0*, 801–802. 2) Zhu, M.; *et al.*, *J. Am. Chem. Soc.*, **2008**, *130*, 5883–5885. 3) Dharmaratne, A. C.; *et al.*, *J. Am. Chem. Soc.*, **2009**, *131*, 13604–13605. 4) Tsukamoto, T.; Yamamoto, K. *et al.*, *Nat. Commun.*, **2018**, *9*, 3873. 5) Kambe, T.; Yamamoto, K. *et al.*, *Nat. Commun.*, **2017**, *8*, 2046. 6) **Muramatsu, H.**; Kambe, T.; Yamamoto, K. *et al.*, *Molecules*, **2022**, *27*, 3398. (**Cover article**)