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Development of Precisely Controlled Structures with Typical Metal Elements for Superatoms

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Metal particles consisting of several or a dozen metal atoms can behave like atoms. These substances, which are called superatoms, are expected to be new building blocks for materials. Although research on superatoms has been developed in theoretical science and synthesized successfully in gas-phase, solution-phase synthesis is still difficult. In this research, solution-phase synthesis of superatoms is investigated via the preparation of metallodendrimers with typical metal elements (Figure 1).[1-3] The solution-phase synthesis of superatoms was achieved by controlling the assembly of various typical metal elements to realize precisely quantitative control of atoms. Based on the assembly of typical metal elements, functional materials such as integrated illuminants and reducing capsules, 13-atom assembly and ratio control of metals were also developed.

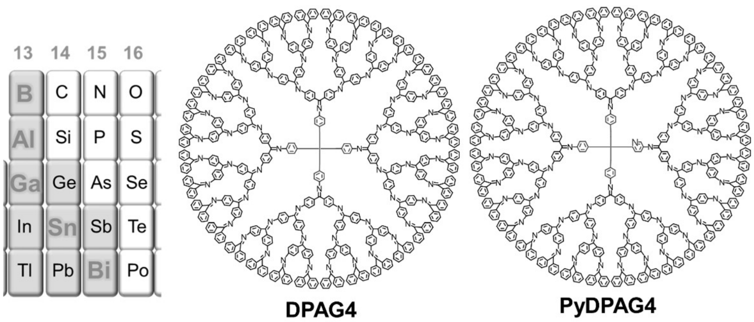

Figure 1. Typical metal elements and structures of DPAs.

(1) Preparation of precisely controlled metallodendrimers with typical metal elements

A 4*th* generation dendrimer (Generation-4 Dendritic Polyphenylazomethines; DPAG4) with phenylazomethine sites on the skeleton possesses a gradient of electron density from the inner to the outer layers due to the π-conjugated branches. The potential gradient enabled the changes of basicity on the phenylazomethine sites which can coordinate with Lewis acidic units stepwisely. In this research, stepwise assembly of various typical metal elements to synthesis superatoms is investigated. In addition, unique functions have also been realized by using bismuth and boron species in DPAG4. Integration of photoluminescent units is achieved by the assembly of bismuth salts.[4] The investigated luminous dendrimers are also developed for the application of solid-state emission and optical switching. A BH_3 assembled dendrimer is found to behave as a reducing capsule.[5] It is useful for the synthesis of ultra-small metal particles due to the multi-electron reduction feature of the assembled reductants.

(2) Development of the controlled assembly

Metal hybrid assembly can be achieved by using the difference of basicity in assembling metal species. Here, the coordination strength and fashion were changed through counter anions of metals.[4c] In addition, finely controlled assembly was developed by using an asymmetrical 4*th* generation dendrimer (PyDPAG4) with a pyridine part in the core. The assembly for PyDPAG4 has realized the control of 1, 1, 3, 2 and 6 units from inner to outer.[1-3] This fine assembly enabled 13-atom assembly and 1-atom doping for the metal particles. Based on these features, full range metal ratio control in a dendrimer was also demonstrated.[6] It was achieved by the reversed metal assembly in solvent conditions. This reversed-order assembly solves the inherent problem of increasing the number of assembled metals at the outer positions of dendrimers.

(3) Synthesis of superatoms in a solution-phase

PyDPAG4, which are similar to DPAG4 skeleton with a pyridine site in the core, was used for the synthesis of Al_{13} superatom. The changes in the UV–vis absorption spectrum during assembling $AlCl_3$ were demonstrated. The spectral change is due to the complex formation, and an observed shift in the isosbestic point reflecting the difference in basicity for imines on each layer of PyDPAG4. This spectral behavior indicates the stepwise assembly starting from the inner imine sites. In particular, the isosbestic point of $AlCl_3$ assembly was clearly different before and after 13 equivalents, indicating the successful assembly of 13 molecules of $AlCl_3$ into the PyDPAG4. Then, the $AlCl_3$ was reduced to prepare a superatom consisting of 13 Al atoms (Figure 2).[1]

According to the superatoms, a three-dimensional periodic table has been proposed considering the superatoms as new building blocks. In order to demonstrate it experimentally, prepared Ga_{13} and Al_{13} superatoms were compared.[2] Both of them are superatoms mimicking halogens in the same valence electrons, however, their electronic properties were found to be different. A newly prepared superatom consisting of three gallium atoms was also investigated through the elucidation of the electronic state and reactivity.

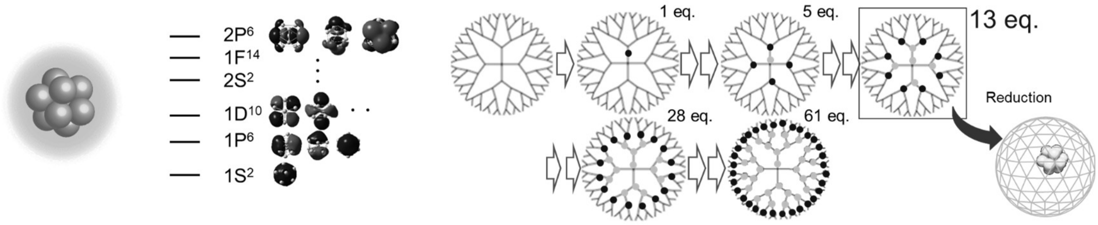

Figure 2. Al_{13} superatom. Superatomic orbitals and a preparation method using a DPA template.

1) T. Kambe, N. Haruta, T. Imaoka, K. Yamamoto, *Nature Commun.* **2017**, *8*, 2046. 2) T. Kambe, A. Watanabe, M. Li, T. Tsukamoto, T. Imaoka, K. Yamamoto, *Adv. Mater.* **2020**, *32*, 1907167. 3) a) T. Kambe, K. Yamamoto, *Polym. J.* **2021**. b) K. Yamamoto, T. Imaoka, M. Tanabe, T. Kambe, *Chem. Rev.* **2020**, *120*, 1397. 4) a) T. Kambe, A. Watanabe, T. Imaoka, K. Yamamoto, *Angew. Chem. Int. Ed.* **2016**, *55*, 13151. b) T. Kambe, T. Imaoka, K. Yamamoto *J. Inorg. Organomet. Polym.* **2018**, *28*, 463. c) T. Kambe, S. Imaoka, T. Imaoka, K. Yamamoto, *J. Nanopart. Res.* **2018**, *20*, 118. d) T. Kambe, R. Hosono, T. Imaoka, K. Yamamoto, *J. Photopolym. Sci. Technol.* **2018**, *31*, 311. e) T. Kambe, S. Imaoka, R. Hasegawa, T. Tsukamoto, T. Imaoka, K. Natsui, Y. Einaga, K. Yamamoto, *J. Inorg. Organomet. Polym.* **2020**, *30*, 169. 5) T. Kambe, T. Imaoka, K. Yamamoto, *Chem. Eur. J.* **2016**, *22*, 16406. 6) T. Kambe, M. Li, T. Takamasa, T. Imaoka, K. Yamamoto, *Chem. Lett.* **2021**, *50*, 1648.