

Targeted Synthesis of Ligand-Protected Gold Superatoms and Exploration of Their Design Principles

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Ligand-protected gold-based clusters $[\text{Au}_x\text{M}_y\text{L}_z]^n$ (M = Group 8, 9, 10, and 11 elements; L = phosphines, thiolates, alkynyls, and halides) are attractive building units of nanoscale materials since they exhibit specific properties and can be treated as stable compounds under ambient conditions. In addition, these clusters having gold-based superatoms in their core mantles provide us with an ideal opportunity to establish the structure-properties correlations within the framework of the superatomic concept.¹⁻⁴ Although increasing number of ligand-protected gold superatoms has been obtained by the conventional synthetic methods based on chemical reduction of the corresponding metal complexes, there is much room for improvement in terms of targetability and selectivity for their synthesis, and controllability for their properties. To tackle the problems, we have focused on two things: (1) development of an efficient synthesis method using pre-formed superatoms as starting materials; (2) controlling the electronic structure of superatoms based on a simple design principle. Our ultimate goal is to add a new dimension to the periodic table by considering the superatoms as artificial elements at the nanoscale (Fig. 1).

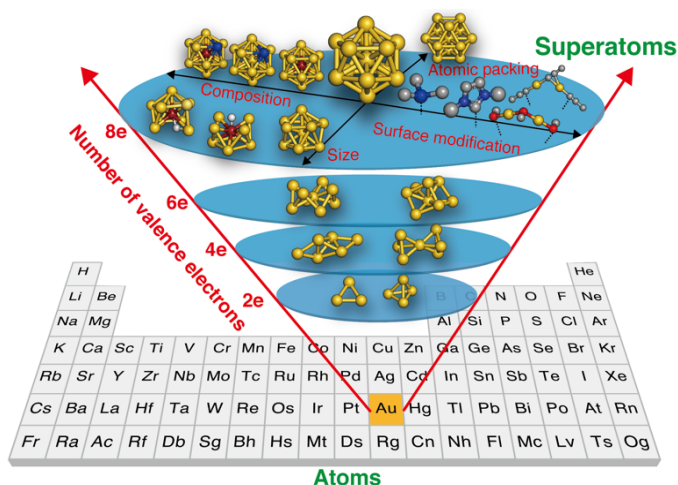


Fig. 1. A new periodic table based on the gold-based superatoms. Reprinted from Ref. 4 with permission. 2021 American Chemical Society.

1. Development of targeted synthesis method of superatoms with atomic precision

Phosphine-protected oblate clusters $[\text{MAu}_8(\text{PPh}_3)_8]^{2+}$ (**MAu₈**; $\text{M} = \text{Au}^+, \text{Pd}, \text{Pt}$) are the prototypical example of 6e superatom and these can be easily synthesized in a gram scale. We have revealed that these superatoms are good starting materials for the atomically-precise transformation reactions; **MAu₈** exhibited a variety of reactions, including core-growth,⁵ ordered alloying,⁶⁻⁸ surface modification,⁹ and dimerization¹⁰ by the

action of hydride (H^-) as an initiator (Fig. 2). The key of success is the role of hydride; it behaves like a two-electron donating dopant and the resultant hydride-doped superatom possesses a high nucleophilicity towards coinage metal complexes. The most notable reaction is the dimerization of two superatoms since the targeted synthesis of an anisotropic structure has been quite difficult so far. This novel synthesis method opens a new avenue to synthesize a multimer of superatoms with good targetability.

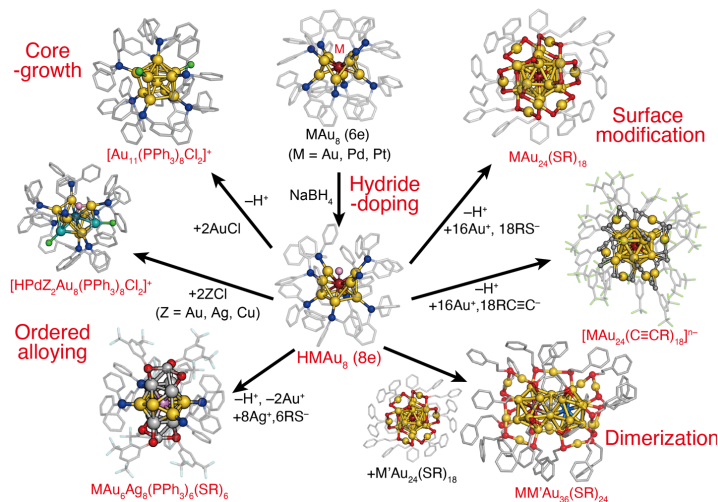


Fig. 2. Atomically-precise transformation reactions of gold superatoms by hydride doping.

2. Exploration of the design principles of gold superatoms

The physicochemical properties of gold superatoms can be modulated by the size, composition, and surface protecting motifs.⁴ This is mainly because of the change in electronic structure of the superatomic core; the absolute energy and the energy gap of superatomic orbitals are changed by the above factors. In order to establish a simple guiding principle to control the electronic structure, we have examined the primitive and deformed jellium model to understand the properties of superatoms. In the jellium model, heterometal dopant provides different formal charge from gold. This causes a change in attractive potential of the valence electrons, giving an energy shift in superatomic orbitals. We have systematically synthesized a variety of doped superatoms^{9,11–13} and the model can qualitatively explain the tendency. This means that the properties of superatoms can be intentionally designed by the simple guiding principles.

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