

LABORATORY OF CATALYTIC CHEMISTRY

Annual Research Highlights

(1) “N-heterocyclic carbene-functionalized magic-number gold nanoclusters”

Here, we report a previously unknown ligand for gold(0) nanoclusters—N-heterocyclic carbenes (NHCs)—which impart high stability to the corresponding gold cluster. The addition of a single NHC to gold nanoclusters results in significantly improved stability and catalytic properties in the electrocatalytic reduction of CO₂. By varying the conditions, nature and number of equivalents of the NHC, predominantly or exclusively monosubstituted NHC-functionalized clusters result.

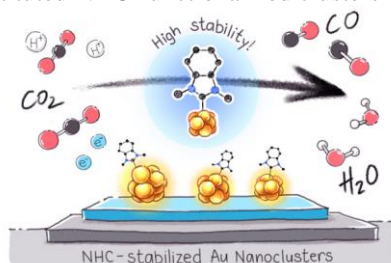


Fig. 1 Highly stable NHC-functionalized Au clusters with improved stability and electrocatalytic reduction of CO₂.

1.(1)-1) *Nature Chem.*, **11**, 419–425 (2019).

(2) “Efficient and Selective Conversion of Phosphine-Protected (MAu₈)²⁺ (M = Pd, Pt) Superatoms to Thiolate-Protected (MAu₁₂)⁶⁺ or Alkynyl-Protected (MAu₁₂)⁴⁺ Superatoms via Hydride Doping”

An efficient and selective method was developed for the synthesis of bimetallic clusters, MAu₂₄L₁₈ (M = Pd or Pt; L = thiolates or alkynyls), by the reaction of Au(I)L oligomers with quasi-spherical [HMAu₈(PPh₃)₈]⁺ superatoms activated by hydride doping. This hydride-mediated conversion produced the novel cluster [PdAu₂₃(ScC₆H₁₁)₁₇]⁰ with a flattened (Pd@Au₁₂)⁶⁺ core, and the new alkynyl-protected clusters [MAu₂₄(C≡CAr^F)₁₈]²⁻ (Ar^F = 3,5-(CF₃)₂C₆H₃) with an icosahedral (M@Au₁₂)⁴⁺ core. This simple and versatile bottom-up approach will provide an opportunity to synthesize a variety of superatoms on a large scale for the promotion of materials science based on superatoms.

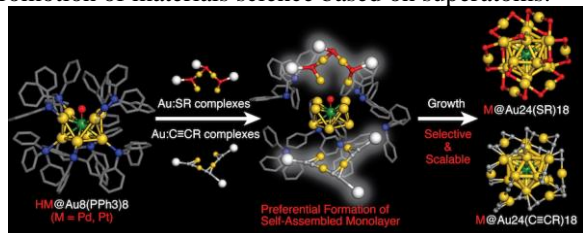


Fig. 2 Hydride-mediated conversion to bimetallic MAu₂₄L₁₈.

1.(1)-2) *J. Am. Chem. Soc.*, **141**, 15994–16002 (2019).

(3) “Elucidating the Doping Effect on the Electronic Structure of Thiolate-Protected Silver Superatoms by Photoelectron Spectroscopy”

Gas-phase photoelectron spectroscopy (PES) was conducted on [XAg₂₄(SPhMe₂)₁₈]⁻ (X = Ag, Au) and [YAg₂₄(SPhMe₂)₁₈]²⁻ (Y = Pd, Pt) with an icosahedral superatomic core, (X@Ag₁₂)⁵⁺ and (Y@Ag₁₂)⁴⁺. PES results show that superatomic orbitals in the (Y@Ag₁₂)⁴⁺ core shift up in energy. The remarkable doping effect of a single Y atom (Y = Pd, Pt) on the electronic structure was theoretically explained as 1) the weaker binding of valence electrons in Y@(Ag⁺)₁₂ due to the reduction in formal charge of the core, and 2) the upward shift of the orbitals by repulsive Coulomb barrier (RCB).

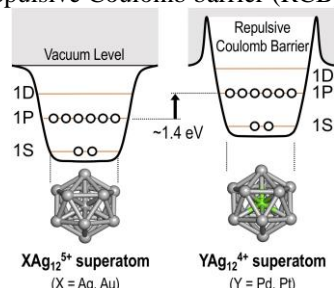


Fig. 3 Shift of energy levels in (X@Ag₁₂)⁵⁺ and (Y@Ag₁₂)⁴⁺ cores due to the charge reduction and RCB.

1.(1)-5) *Angew. Chem., Int. Ed.*, **58**, 11637–11641 (2019).

(4) “Structural Evolution of Iridium Oxide Cluster Anions Ir_nO_m⁻ (n = 5–8) with Sequential Oxidation: Binding Mode of O Atoms and Ir Framework”

Geometric structures of small cluster anions of iridium oxide Ir_nO_m⁻ (n = 5–8, m = 0–14) were investigated by ion mobility mass spectrometry and theoretical calculation to clarify the evolutionary behavior of the binding modes of the O atoms and the Ir frameworks as a function of m. For n = 8, the O atoms are sequentially bonded to terminal sites of the cubic and deformed Ir₈ frameworks for m = 1–6 and m = 7–11, respectively. At m ≥ 11, Ir–Ir bonds in the Ir framework were broken.

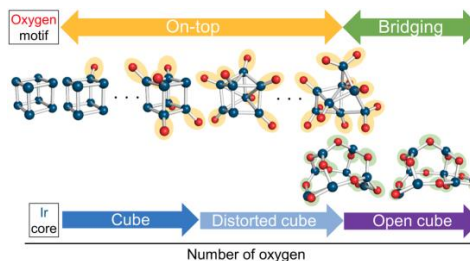


Fig. 4 Structural evolution of Ir_nO_m⁻ (n = 5–8, m = 0–14).

1.(1)-8) *J. Phys. Chem. C*, **123**, 15301–15306 (2019).

化学反応学研究室

研究ハイライト

(1) N-ヘテロ環カルベン保護魔法数金クラスター

[Au₁₁(PPh₃)₈Cl₂]⁺クラスターのPPh₃配位子の一部をN-ヘテロ環カルベン(NHC)配位子で置換することにより、Auクラスターに高い安定性とCO₂の電気化学的還元反応に対する触媒活性を付与できた。

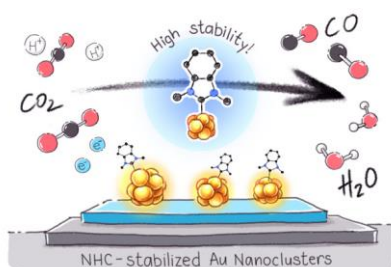


図1 CO₂の電気化学的還元反応に触媒活性を示す、安定なNHC保護Auクラスター

1.(1)-1) *Nature Chem.*, **11**, 419–425 (2019).

(2) ホスフィン保護 (MAu₈)²⁺ (M = Pd, Pt) 超原子のチオラート保護 (MAu₁₂)⁶⁺およびアルキニル保護 (MAu₁₂)⁴⁺超原子への高効率・高選択的変換

ヒドリドをドーピングして活性化した超原子 [HMAu₈(PPh₃)₈]⁺ (M = Pd, Pt) と Au(I)L (L = チオラート, アルキニル) の反応により, MAu₂₄L₁₈ 合金クラスターを高効率・高選択的に合成する方法を開発した。この方法により, 扁平な (Pd@Au₁₂)⁶⁺ コアをもつ [PdAu₂₃(ScC₆H₁₁)₁₇]⁰ や正二十面体型(M@Au₁₂)⁴⁺ コアをもつ [MAu₂₄(C≡CAr^F)₁₈]²⁻ (Ar^F = 3,5-(CF₃)₂C₆H₃) といった新奇 Au クラスターが合成できた。

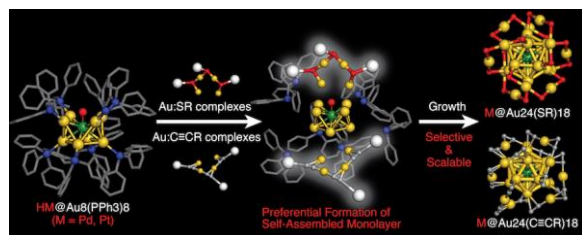


図2 ヒドリド付加体を経由する MAu₂₄L₁₈ への変換反応
1.(1)-2) *J. Am. Chem. Soc.*, **141**, 15994–16002 (2019).

(3) 光電子分光法によるチオラート保護銀超原子の電子構造に対するドーピング効果の解明

液相合成した正二十面体型の(X@Ag₁₂)⁵⁺および(Y@Ag₁₂)⁴⁺をコアとする[XAg₂₄(SPhMe₂)₁₈]⁺ (X = Ag, Au) および[YAg₂₄(SPhMe₂)₁₈]²⁻ (Y = Pd, Pt) に, 気相光電子分光法(PES)を適用した。Y原子のドーピング効果として1) 電子親和力の減少と2) クーロン障壁(RCB)による軌道の上昇が観測された。

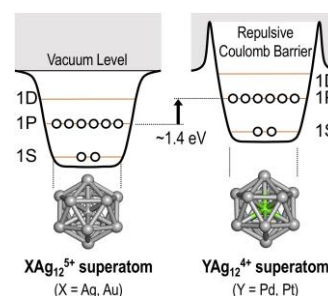


図3 RCBによる(M@Ag₁₂)⁴⁺のエネルギー準位のシフト
1.(1)-5) *Angew. Chem., Int. Ed.*, **58**, 11637–11641 (2019).

(4) 段階的な酸化による酸化イリジウムクラスター Ir_nO_m⁻ (n = 5–8, m = 0–14) の構造変化: Ir 骨格と O 原子の結合様式

イオン移動度質量分析法と理論計算から, 酸化イリジウムクラスター Ir_nO_m⁻ (n = 5–8, m = 0–14) の幾何構造を調べた。n = 8 では O 原子の結合位置が頂点から架橋型に変化すると, Ir 骨格が立方体型から変形していくことを明らかにした。

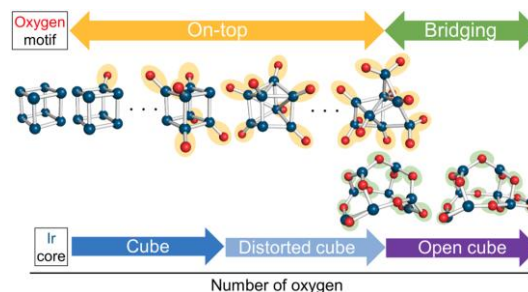


図4 Ir_nO_m⁻ (n = 5–8, m = 0–14) の構造変化
1.(1)-8) *J. Phys. Chem. C*, **123**, 15301–15306 (2019).

1. 原著論文

(1) Refereed Journals

- 1) M. R. Narouz, K. M. Osten, P. J. Unsworth, R. W. Y. Man, K. Salorinne, S. Takano, R. Tomihara, S. Kaappa, S. Malola, C.-T. Dinh, J. D. Padmos, K. Ayoo, P. J. Garrett, M. Nambo, J. H. Horton, E. H. Sargent, H. Häkkinen, T. Tsukuda, C. M. Crudden, “N-heterocyclic carbene-functionalized magic-number gold nanoclusters”, *Nat. Chem.* **11**, 419–425 (2019).
- 2) S. Takano, S. Ito, T. Tsukuda, “Efficient and Selective Conversion of Phosphine-Protected (MAu₈)²⁺ (M = Pd, Pt) Superatoms to Thiolate-Protected (MAu₁₂)⁶⁺ or Alkynyl-Protected (MAu₁₂)⁴⁺ Superatoms via Hydride Doping”, *J. Am. Chem. Soc.*, **141**, 15994–16002 (2019).
- 3) M. R. Narouz, S. Takano, P. A. Lummis, T. I. Levchenko, A. Nazemi, S. Kaappa, S. Malola, G. Yousefalizadeh, L. A. Calhoun, K. G. Stamplecoskie, H. Häkkinen, T. Tsukuda, C. M. Crudden, “Robust, Highly Luminescent Au₁₃ Superatoms Protected by N-Heterocyclic Carbenes”, *J. Am. Chem. Soc.*, **141**, 14997–15002 (2019).
- 4) M. Suyama, S. Takano, T. Nakamura, T. Tsukuda, “Stoichiometric Formation of Open-Shell [PtAu₂₄(SC₂H₄Ph)₁₈]⁻ via Spontaneous Electron Proportionation between [PtAu₂₄(SC₂H₄Ph)₁₈]²⁻ and [PtAu₂₄(SC₂H₄Ph)₁₈]⁰”, *J. Am. Chem. Soc.*, **141**, 14048–14051 (2019).
- 5) K. Kim, K. Hirata, K. Nakamura, H. Kitazawa, S. Hayashi, K. Koyasu, T. Tsukuda, “Elucidating the Doping Effect on the Electronic Structure of Thiolate-Protected Silver Superatoms by Photoelectron Spectroscopy”, *Angew. Chem., Int. Ed.*, **58**, 11637–11641 (2019).
- 6) S. Ito, S. Takano, T. Tsukuda, “Alkynyl-Protected Au₂₂(C≡CR)₁₈ Clusters Featuring New Interfacial Motifs and R-dependent Photoluminescence”, *J. Phys. Chem. Lett.*, **10**, 6892–6896 (2019).
- 7) K. Hirano, S. Takano, T. Tsukuda, “Asymmetric Aerobic Oxidation of Secondary Alcohols Catalyzed by Poly(*N*-vinyl-2-pyrrolidone)-stabilized Gold Clusters Modified with Cyclodextrin Derivatives”, *Chem. Commun.*, **55**, 15033–15036 (2019).
- 8) R. Tomihara, K. Koyasu, T. Nagata, J. W. J. Wu, M. Nakano, K. Ohshimo, F. Misaizu, T. Tsukuda, “Structural Evolution of Iridium Oxide Cluster Anions Ir_nO_m⁻ (n = 5–8) with Sequential Oxidation: Binding Mode of O Atoms and Ir Framework”, *J. Phys. Chem. C*, **123**, 15301–15306 (2019).
- 9) K. Hirata, K. Kim, K. Nakamura, H. Kitazawa, S. Hayashi, K. Koyasu, T. Tsukuda, “Photoinduced Thermoionic Emission from [M₂₅(SR)₁₈]⁻ (M = Au, Ag) Revealed by Anion Photoelectron Spectroscopy”, *J. Phys. Chem. C*, **123**, 13174–13179 (2019).
- 10) T. Omoda, S. Takano, T. Tsukuda, “Reduction-Resistant [Au₂₅(cyclohexanethiolate)₁₈]⁰ with an Icosahedral Au₁₃ Core”, *Chem. Lett.*, **48**, 885–887 (2019).
- 11) R. Takahata, T. Tsukuda, “Ultrathin Gold Nanowires and Nanorods”, *Chem. Lett.* **48**, 906–915 (2019).
- 12) H. Hirai, S. Takano, T. Tsukuda, “Synthesis of trimetallic (HPd@M₂Au₈)³⁺ superatoms (M = Ag, Cu) via hydride-mediated regioselective doping to (Pd@Au₈)²⁺”, *ACS Omega*, **4**, 7070–7075 (2019).
- 13) S. Muramatsu, T. Tsukuda, “Reductive Activation of Small Molecules by Anionic Coinage Metal Atoms and Clusters in the Gas Phase”, *Chem. Asian J.*, **14**, 3763–3772 (2019).
- 14) C.-F. Chang, H. Kuramochi, M. Singh, R. Abe-Yoshizumi, T. Tsukuda, H. Kandori, T. Tahara, “Acid-Base Equilibrium of the Chromophore Counterion Results in Distinct Photoisomerization Reactivity in the Primary Event of Proteorhodopsin”, *Phys. Chem. Chem. Phys.*, **21**, 25728–25734 (2019).

2. 総説・解説

- 1) R. Jin, Y. Pei, T. Tsukuda, “Controlling Nanoparticles with Atomic Precision”, *Acc. Chem. Res.*, **52**, 1 (2019).
- 2) K. Hirata, R. Tomihara, K. Kim, K. Koyasu, T. Tsukuda, “Characterization of Chemically Modified Gold and Silver Clusters in Gas Phase”, *Phys. Chem. Chem. Phys.*, **21**, 17463–17474 (2019).
- 3) S. Yamazoe, T. Tsukuda, “X-Ray Absorption Spectroscopy on Atomically Precise Metal Clusters”, *Bull. Chem. Soc. Jpn.*, **92**, 193–204 (2019).
- 4) 陶山めぐみ・高野慎二郎・中村敏和・佃達哉：「クラスター間の自発的電子移動による開殻系クラスター[PtAu₂₄(SC₂H₄Ph)₁₈]の化学量論的生成」, *ナノ学会会報*, **18**, 21–26 (2019).
- 5) 佃達哉：「化学修飾された超原子の構造—ナノスケールの人工原子と擬似分子の創成に向けて」, *Mol. Sci.*, **13**, 14048–14051 (2019).
- 6) 山添誠司・佃達哉：「X線吸収分光法による配位子保護金属クラスターの構造・結合の硬さ評価」, *ナノ学会会報*, **17**, 43–47 (2019).

3. 著書

- 1) K. Koyasu, K. Hirata, T. Tsukuda: “Characterization of Chemically Modified Gold/Silver Superatoms in the Gas Phase”, edited by T. Ebata and M. Fujii (Springer, 2019), pp. 223–253.