LABORATORY OF CATALYTIC CHEMISTRY

Annual Research Highlights

(1) "Critical Role of CF_3 Groups in the Electronic Stabilization of $[PdAu_{24}(C{\equiv}C_6H_3(CF_3)_2)_{18}]^{2-}$ as Revealed by Gas-Phase Anion Photoelectron Spectroscopy"

The role of alkynyl ligands with CF_3 group in the stability of metal clusters was investigated by gas-phase anion photoelectron spectroscopy (PES) on $[PdAu_{24}(C{\equiv}C_6H_3(CF_3)_2)_{18-x}(C{\equiv}CPh)_x]^{2-}$. PES on the cluster anions with specific x (= 0–6) revealed that electron binding energies decreased linearly with x, indicating the CF_3 substituents on the alkynyl ligand played a critical role in the electronic stabilization of the cluster.

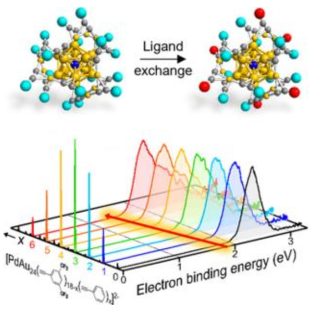

Fig. 1 Linear change of electron binding energies by replacing the alkynyl ligands with CF_3 group to those without CF_3 observed by gas-phase anion photoelectron spectroscopy.

1.(1)-2) *J. Phys. Chem. Lett.* **12**, 10417–10421 (2021).

(2) "Photoluminescence of Doped Superatoms $M@Au_{12}$ (M = Ru, Rh, Ir) Homoleptically Capped by $(Ph_2)PCH_2P(Ph_2)$: Efficient Room-Temperature Phosphorescence from $Ru@Au_{12}$"

A series of doped gold superatoms $M@Au_{12}$ (M = Ru, Rh, Ir) was synthesized by capping with the bidentate ligand $(Ph_2)PCH_2P(Ph_2)$. The $Ru@Au_{12}$ exhibited a room-temperature phosphorescence with the highest quantum yield of 0.37 in deaerated dichloromethane. Density functional theory calculations suggested that the phosphorescence is ascribed to a rapid intersystem crossing due to the similarity between the singlet and triplet excited states in terms of structure and energy.

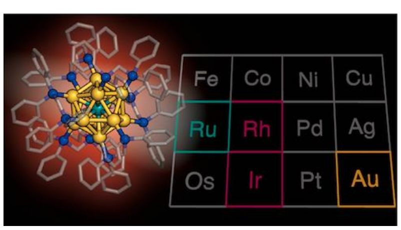

Fig. 2 Efficient phosphorescence from $Ru@Au_{12}$ homoleptically capped by $(Ph_2)PCH_2P(Ph_2)$.

1.(1)-7) *J. Am. Chem. Soc.*, **143**, 10560–10564 (2021).

(3) "New Magic Au_{24} Cluster Stabilized by PVP: Selective Formation, Atomic Structure, and Oxidation Catalysis"

$Au_{24}Cl_x$ (x = 0–3), was selectively synthesized by the kinetically controlled reduction in a microfluidic mixer in the presence of poly(*N*-vinyl-2-pyrrolidone) (PVP). The atomic structure of the PVP-stabilized $Au_{24}Cl_x$ was investigated by aberration-corrected transmission electron microscopy and density functional theory calculations. The $Au_{24}Cl_x$:PVP clusters catalyzed the aerobic oxidation of benzyl alcohol derivatives.

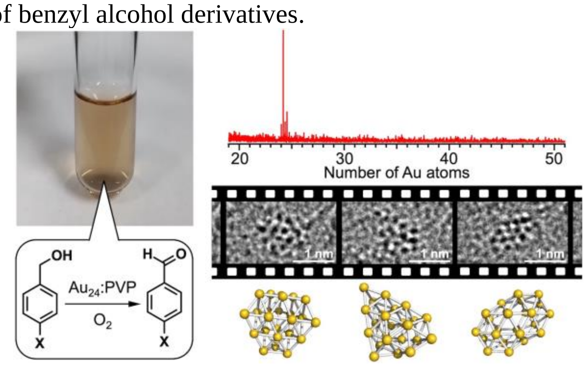

Fig. 3 Selective synthesis of new magic Au_{24} cluster stabilized by PVP with structures observed in ACTEM video imaging.

1.(1)-10) *JACS Au*, **1**, 660–668 (2021).

(4) "Controlled Dimerization and Bonding Scheme of Icosahedral $M@Au_{12}$ (M = Pd, Pt) Superatoms"

Targeted syntheses of $MM'Au_{36}(PET)_{24}$ (M, M′=Pd, Pt; PET=SC_2H_4Ph) were achieved by hydride-mediated fusion reactions between $[MAu_8(PPh_3)_8]^{2+}$ and $[M'Au_{24}(PET)_{18}]^{-}$. Despite small number of valence electrons (12 e) of $MM'Au_{21}$, the distances between the icosahedrons were larger than that in the bi-icosahedral Au_{23} core of $Au_{38}(PET)_{24}$ (14 e). These counterintuitive results were explained by a "bent bonding model" based on tilted bonding interaction between the 1P superatomic orbitals of $M@Au_{12}$ and $M'@Au_{12}$ superatoms.

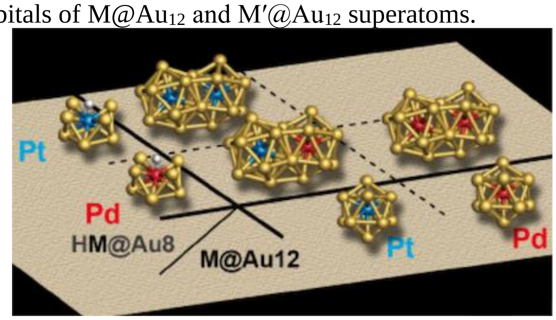

Fig. 4 Superatomic molecules $MM'Au_{21}$ (M, M′=Pd, Pt) with biicosahedral motifs synthesized by hydride-mediated fusion reactions of superatoms.

1.(1)-14) *Angew. Chem. Int. Ed.*, **60**, 645–649 (2021).

化学反応学研究室

研究ハイライト

(1) 気相光電子分光による$[PdAu_{24}(C{\equiv}C_6H_3(CF_3)_2)_{18}]^{2-}$の電子的安定化に対する$CF_3$基の効果の解明

$[PdAu_{24}(C{\equiv}C_6H_3(CF_3)_2)_{18-x}(C{\equiv}CPh)_x]^{2-}$に対して気相光電子分光を用いることで、$x$が増加するにつれて電子束縛エネルギーが線形に低下することを見出した。これはアルキニル配位子上のCF_3基が本クラスターの電子的安定化に寄与することを示している。

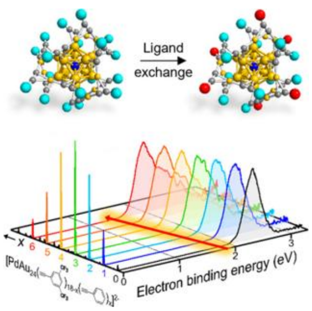

図１ 配位子を置換した際の気相光電子スペクトルと電子束縛エネルギーの線形変化
1.(1)-2) *J. Phys. Chem. Lett.* **12**, 10417–10421 (2021).

(2) ジホスフィン配位子で保護された$M@Au_{12}$ (M = Ru, Rh, Ir)超原子の発光特性：$Ru@Au_{12}$超原子における高効率室温リン光

ジホスフィン配位子 $((Ph_2)PCH_2P(Ph_2))$ で保護された$M@Au_{12}$ (M = Ru, Rh, Ir) 超原子を合成して発光特性を調査したところ、$Ru@Au_{12}$超原子が室温・脱気ジクロロメタン中において量子収率 0.37 に達する高効率なリン光を示した。この理由として、一重項および三重項励起状態の構造およびエネルギーの類似による項間交差の促進を量子化学計算の結果から提案した。

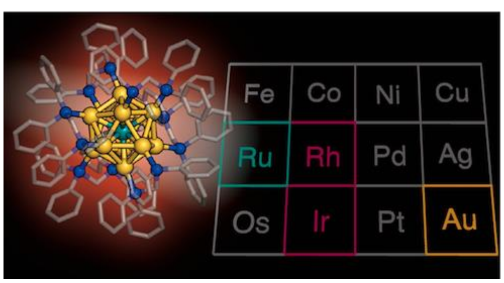

図２ ジホスフィン配位子で保護された $M@Au_{12}$ (M = Ru, Rh, Ir)超原子の発光特性
1.(1)-7) *J. Am. Chem. Soc.*, **143**, 10560–10564 (2021).

(3) PVP で保護された新規魔法数Au_{24}クラスター：選択合成、構造解析および酸化触媒特性

均一溶液混合を用い，高濃度 PVP 中で還元速度を制御して、選択的に$Au_{24}Cl_x$ (x = 0–3)を合成することに成功した。収差補正 TEM の動画観察とシミュレーションを組み合わせ、その構造が量子化学計算から推定される構造と一致することを観察した。また、$Au_{24}Cl_x$:PVP がベンジルアルコール誘導体の酸化反応に触媒活性を示すことを見出した。

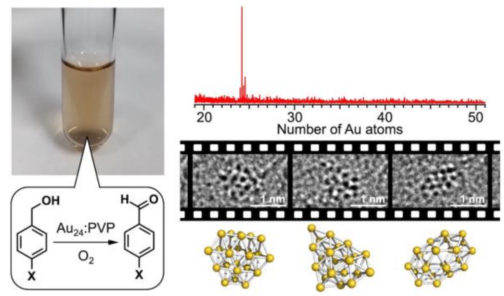

図３ Au_{24}クラスターの選択合成と収差補正 TEM での動画観察を用いた構造解析
1.(1)-10) *JACS Au*, **1**, 660–668 (2021).

(4) 正 20 面体$M@Au_{12}$ (M = Pd, Pt) 超原子の選択的二量化と結合様式解明

$[MAu_8(PPh_3)_8]^{2+}$クラスターへのヒドリドドープを介した$[M'Au_{24}(PET)_{18}]^-$クラスターとの融合反応によって$MM'Au_{36}(PET)_{24}$ (M, M′ = Pd, Pt; PET = SC_2H_4Ph)を意図的に合成することに成功した。14 個の価電子を持つAu_{23}超原子分子と比べて、価電子が 12 個である$MM'Au_{21}$超原子分子は、想定される結合次数の高さに反して各超原子中心間の距離が長くなっていた。この予想に反した結果は、1P 超原子軌道間の傾斜した結合相互作用に基づく「湾曲結合モデル」によって説明できると結論付けた。

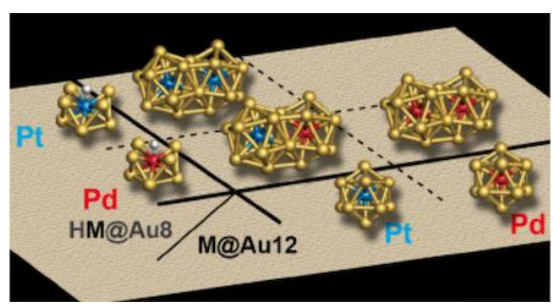

図４ ヒドリドドープを介した超原子の融合反応による正 20 面体二量体超原子分子$MM'Au_{21}$ (M, M′=Pd, Pt) の合成
1.(1)-14) *Angew. Chem. Int. Ed.*, **60**, 645–649 (2021).

1. 原著論文

(1) Refereed Journals

1) T. Omoda, S. Takano, S. Masuda, T. Tsukuda, "Decorating an anisotropic Au_{13} core with dendron thiolates: enhancement of optical absorption and photoluminescence", *Chem. Commun.*, **57**, 12159–12162 (2021).
2) S. Ito, K. Koyasu, S. Takano, T. Tsukuda, "Critical Role of CF_3 Groups in the Electronic Stabilization of $[PdAu_{24}(C{\equiv}C_6H_3(CF_3)_2)_{18}]^{2-}$ as Revealed by Gas-Phase Anion Photoelectron Spectroscopy", *J. Phys. Chem. Lett.*, **12**, 10417–10421 (2021).
3) X. Li, S. Takano, T. Tsukuda, "Ligand Effects on the Hydrogen Evolution Reaction Catalyzed by Au_{13} and $Pt@Au_{12}$: Alkynyl vs Thiolate", *J. Phys. Chem. C*, **125**, 23226–23230 (2021).
4) S. Emori, S. Takano, K. Koyasu, Tsukuda, "Chemical Transformations of $[MAu_8(PPh_3)_8]^{2+}$ (M = Pt, Pd) and $[Au_9(PPh_3)_8]^{3+}$ in Methanol Induced by Irradiation of Atmospheric Pressure Plasma", *J. Chem. Phys.*, **155**, 124312 (2021).
5) S. Matsuda, S. Masuda, S. Takano, N. Ichikuni, T. Tsukuda, "Synergistic Effect in Ir- or Pt-Doped Ru Nanoparticles: Catalytic Hydrogenation of Carbonyl Compounds under Ambient Temperature and H_2 Pressure", *ACS Catal.*, **11**, 10502–10507 (2021).
6) N. Shinjo, S. Takano, T. Tsukuda, "Effects of π-Electron Systems on Optical Activity of Au_{11} Clusters Protected by Chiral Diphosphines", *Bull. Korean Chem. Soc.*, **42**, 1265–1268 (2021).
7) S. Takano, H. Hirai, T. Nakamura, T. Iwasa, T. Taketsugu, T. Tsukuda, "Photoluminescence of Doped Superatoms $M@Au_{12}$ (M = Ru, Rh, Ir) Homoleptically Capped by $(Ph_2)PCH_2P(Ph_2)$: Efficient Room-Temperature Phosphorescence from $Ru@Au_{12}$", *J. Am. Chem. Soc.*, **143**, 10560–10564 (2021).
8) S. Takano, T. Tsukuda, "Atomically-Ordered Trimetallic Superatoms $M@Au_6Ag_6$ (M = Pd, Pt): Synthesis and Photoluminescence Properties", *Chem. Lett.*, **50**, 1419–1422 (2021).
9) K. Hirano, S. Takano, T. Tsukuda, "Ligand Effects on the Structures of $[Au_{23}L_6(C{\equiv}CPh)_9]^{2+}$ (L = N-Heterocyclic Carbene vs Phosphine) with Au_{17} Superatomic Cores", *J. Phys. Chem. C*, **125**, 9930–9936 (2021).
10) S. Hasegawa, S. Takano, K. Harano, T. Tsukuda, "New Magic Au_{24} Cluster Stabilized by PVP: Selective Formation, Atomic Structure, and Oxidation Catalysis", *JACS Au*, **1**, 660–668 (2021).
11) S. Osugi, S. Takano, S. Masuda, K. Harano, T. Tsukuda, "Few-nm-Sized, Phase-Pure Au_5Sn Intermetallic Nanoparticles: Synthesis and Characterization", *Dalton Trans.*, **50**, 5177–5183 (2021).
12) T. Tsukuda, H. Häkkinen, "The Journal of Physical Chemistry C Virtual Special Issue on Metal Clusters, Nanoparticles, and the Physical Chemistry of Catalysis", *J. Phys. Chem. C*, **125**, 4927–4929 (2021).
13) S. Yamazoe, A. Yamamoto, S. Hosokawa, R. Fukuda, K. Hara, M. Nakamura, K. Kamazawa, T. Tsukuda, H. Yoshida, T. Tanaka, "Identification of Hydrogen Species on Pt/Al_2O_3 by in situ Inelastic Neutron Scattering and Their Reactivity with Ethylene", *Catal. Sci. Technol.*, **11**, 116–123 (2021).
14) E. Ito, S. Takano, T. Nakamura, T. Tsukuda, "Controlled Dimerization and Bonding Scheme of Icosahedral $M@Au_{12}$ (M = Pd, Pt) Superatoms", *Angew. Chem. Int. Ed.*, **60**, 645–649 (2021).

2. 総説・解説

1) K. Koyasu, T. Tsukuda, "Gas-Phase Studies of Chemically Synthesized Au and Ag Clusters", *J. Chem. Phys.*, **154**, 140901 (2021).
2) S. Takano, T. Tsukuda, "Chemically Modified Gold/Silver Superatoms as Artificial Elements at Nanoscale:

Design Principles and Synthesis Challenges", *J. Am. Chem. Soc.*, **143**, 1683–1698 (2021).
3) S. Hasegawa, T. Tsukuda, "Exploring Novel Catalysis Using Polymer-Stabilized Metal Clusters", *Bull. Chem. Soc. Jpn.*, **94**, 1036–1044 (2021).
4) T. Omoda, S. Takano, T. Tsukuda, "Toward Controlling the Electronic Structures of Chemically Modified Superatoms of Gold and Silver", *Small*, **17**, 2001439 (2021).
5) S. Takano, T. Tsukuda, "Atomically-precise synthesis of chemically-modified superatoms", *Superatoms: Principles, Synthesis, and Applications,* ed. P. Jena and Q. Sun (Wiley, 2021), page 141-181.