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Author(s)	Shichibu, Yukatsu; Kamei, Yutaro; Konishi, Katsuaki
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Unique [core+two] structure and optical property of dodeca-ligated undecagold cluster: Critical contribution of the exo gold atoms to the electronic structure†

Yukatsu Shichibu, Yutaro Kamei, and Katsuaki Konishi*

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A novel dodeca-ligated undecagold cluster having a nonagold core plus two exo-attached gold atoms was synthesized. Unlike the conventional icosahedron-based “core-only” isomer, the [9+2] cluster showed an intense visible absorption band. Theoretical calculation showed the involvement of the exo gold atoms in the generation of the unique electronic structure.

For several decades, there has been considerable interest in the unique structures and properties of geometrically defined gold clusters.^{1,2} The crystal structures of many phosphine-protected clusters have been determined;^{1,3-6} they reveal the metallic moieties generally prefer to form a “core” consisting of fused polyhedra. Herein we report the unusual [core+two] structure of a novel diphosphine-coordinated cluster cation [Au₁₁(Ph₂P(CH₂)₂PPh₂)₆]³⁺ (**1**), whose Au₁₁ moiety consists of a toroidal Au₉ core and two appended gold atoms. The optical profile of **1** was rather different from those of conventional “core-only” clusters, and was characterised by the intense isolated absorption band in the visible region. We also conducted theoretical calculation studies⁷ to demonstrate the critical role of the exo-attached gold atoms in the generation of the unique electronic structure.

The dodeca-ligated Au₁₁ cluster cation (**1**) was synthesized from the gold complex Au₂(Ph₂P(CH₂)₂PPh₂)Cl₂.⁸ When the gold salt was reduced by NaBH₄ in ethanol at 0 °C, the colourless solution gradually became greenish over time. The addition of NaSbF₆ after 1 h precipitated the cluster product as the hexafluoroantimonate salt, which was further purified by recrystallisation. The electrospray ionization mass spectrum of the cluster species thus obtained shows a set of signals around m/z ≈ 1519, which was unambiguously assigned to the trivalent cluster cation

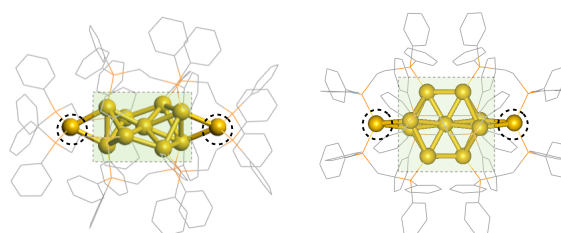


Fig. 1 Side (left) and top (right) views of the crystal structure of [Au₁₁(Ph₂P(CH₂)₂PPh₂)₆]³⁺ (**1**) representing the [9+2] structure consisting of a Au₉ core and two gold atoms at the exo positions. The core units and the exo gold atoms are indicated by the shaded rectangles and the dotted circles, respectively.

[Au₁₁(Ph₂P(CH₂)₂PPh₂)₆]³⁺ by comparison with a simulated isotopic distribution pattern (see, ESI†). Single-crystal X-ray analysis of **1**·(SbF₆)₃ revealed a unique cluster structure composed of a Au₉ core plus two gold atoms at the exo positions (Fig. 1). The exo atoms form triangles by sharing an edge of the Au₉ core. The Au₉ core unit is apparently similar to previously known examples of butterfly-shaped clusters, although it has a slightly wider range of Au–Au bond distances (2.6294(8)–2.9709(8) Å) than [Au₉(PPh₃)₈]³⁺ (2.6745(9)–2.8804(12) Å)^{3b} and [Au₉(P(*p*-C₆H₄OCH₃)₃)₈]³⁺ (2.689(2)–2.899(4) Å).^{3a} This may reflect some distortion caused by the bridging of the exo gold atoms. The exo gold atoms have Au–Au bond distances of 2.7769(9) and 2.8240(8) Å, which lie in the range of the bond distances in the central butterfly unit. Each of the exo gold atoms of **1** is bonded to the two phosphine ligands and is situated at the tetrahedral centre, whereas the eight peripheral gold atoms of the Au₉ core accommodate single phosphine ligands. The structure found in the solid state appeared essentially retained in solution. The ³¹P NMR spectrum of **1**·(SbF₆)₃ in CD₂Cl₂ showed three signals with an intensity ratio of 1:1:1 (Figure S2, ESI†), which were in agreement with the crystal structure.

1·(SbF₆)₃ in dichloromethane was deep green in colour. Accordingly, the electronic absorption spectrum revealed a distinct band in the red region (663 nm) together with small humps in the blue to UV region (460 and 390 nm) (Fig. 2a). The intense low-energy absorption at 663 nm ($\epsilon_{\text{max}} = 8.9 \times 10^4 \text{ L} \cdot \text{cm}^{-1} \cdot \text{mol}^{-1}$) was apparently observed as a single isolated

Faculty of Environmental Earth Science, Hokkaido University, North 10 West 5, Sapporo 060-0810, Japan. Fax: +81 11 7064538; Tel: +81 11 7064538; E-mail: konishi@ees.hokudai.ac.jp

† Electronic Supplementary Information (ESI) available: Experimental procedures, characterization and crystallographic data, and details of DFT calculations. CCDC 862706. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc30251a

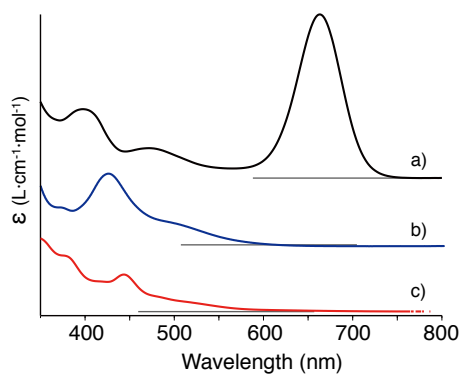


Fig. 2 Visible absorption spectra of a) $[\text{Au}_{11}(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)_6]^{3+}$ (**1**), b) $[\text{Au}_{11}(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)_5]^{3+}$ (**2**) and c) $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$.

band, suggesting that it arises from a specific optical transition. In contrast, the deca-ligated Au_{11} isomer with an icosahedron-based core structure, which is frequently found in the phosphine-coordinated gold cluster family,^{4,13} exhibited a completely different absorption spectrum. For example, $[\text{Au}_{11}(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)_5]^{3+}$ (**2**)^{4c} had a relatively weak absorption band at a high energy (425 nm) that overlapped a broad tail that decreased monotonically toward the red region (Fig. 2b). Such tail and humps spectral characteristics are ubiquitously observed for conventional “closed” gold clusters such as Au_{13} and Au_{25} that have icosahedron-based cores.^{1,5} It should be noted that $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$, which has a toroidal Au_9 core and thus can be a model of the central substructure of **1**,⁹ had a similar tail-and-humps spectrum (c). Therefore, the gold atoms at the exo positions are likely to participate in the generation of the unique visible absorption of **1**.

To obtain further insights into the correlation of optical property and geometrical structure, we performed quantum chemical calculations with the TURBOMOLE package.¹⁰ Fig. 3a (middle) shows the calculated energies of Kohn–Sham molecular orbitals (MOs) and the atomic orbital contributions of $[\text{Au}_{11}(\text{H}_2\text{P}(\text{CH}_2)_2\text{PH}_2)_6]^{3+}$ (**1'**) based on the crystal structure of **1**. In the electronic structure, HOMO, HOMO–1, and LUMO through LUMO+7 are preferentially composed of the 6sp atomic orbitals of gold (green, Fig. 3a), thus forming the sp-band. The HOMO and the LUMO had appreciably different energies from their adjacent orbitals (HOMO–1 and LUMO+1, respectively). Fig. 3a (bottom, solid line) shows the theoretical absorption spectrum simulated by performing time-dependent density functional theory (TDDFT) calculation. The first (lowest-energy) excitation due to the intraband (sp → sp) HOMO → LUMO transition occurred at 2.20 eV (564 nm). This transition was dominant in the oscillator strength (see, ESI†) and was observed as an isolated band in the simulated spectrum. It is thus assigned to the intense band at 663 nm of **1** (Fig. 2a and Fig. 3a (bottom, dotted line)). The higher-energy transitions, such as HOMO–1 → LUMO+2 (3.10 eV) and HOMO–2 → LUMO+4 (3.64 eV), contribute to the generation of the two absorption bands between 300 and 450 nm, which are likely to correspond to the relatively weak humps at 460 and 390 nm in the spectrum of **1**. Overall, the simulated spectrum of **1'** agrees well with the experimental spectrum of **1**, especially its spectral shape.

In contrast, the electronic structure of the spherical Au_{11}

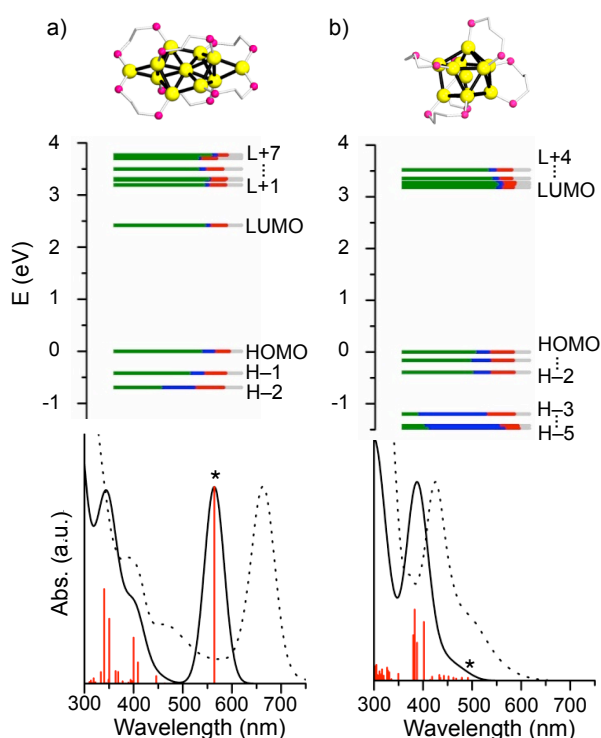


Fig. 3 Geometrical structures (top, Au and P atoms highlighted in yellow and magenta, respectively), Kohn–Sham (KS) orbital energy level diagrams (middle), and theoretical absorption spectra (bottom, solid lines) of a) $[\text{Au}_{11}(\text{H}_2\text{P}(\text{CH}_2)_2\text{PH}_2)_6]^{3+}$ (**1'**) and b) $[\text{Au}_{11}(\text{H}_2\text{P}(\text{CH}_2)_3\text{PH}_2)_5]^{3+}$ (**2'**). Each KS orbital is relative to the HOMO energy and is drawn to indicate the relative contributions (line length with color labels) of the atomic orbitals of Au (6sp) in green, Au (5d) in blue, P (3p) in red, and miscellaneous in gray. H–X and L+Y represent HOMO–X and LUMO+Y, respectively. Experimental absorption profiles of **1** and **2** (dotted lines) are shown for comparison. The asterisks indicate the HOMO–LUMO transitions.

cluster $[\text{Au}_{11}(\text{H}_2\text{P}(\text{CH}_2)_3\text{PH}_2)_5]^{3+}$ (**2'**) differed remarkably. The HOMO and the LUMO were not so energetically isolated from their neighboring orbitals (Fig. 3b (middle)). The LUMO to LUMO+4 were, though not degenerate, very close to each other. The TDDFT results reveal that the oscillator strength of the HOMO → LUMO transition (2.52 eV, 491 nm) was small and close to those of several transitions with similar energies (see, ESI†). Transitions with significant oscillator strengths were found at higher energies (e.g., 3.24 eV, 383 nm), thereby giving rise to the tail-plus-humps profile (Fig. 3b (bottom, solid line)). This trend was reasonably well reproduced in the experimentally observed spectrum (Fig. 2b and Fig. 3b (bottom, dotted line)).

As described above, the HOMO–LUMO transition is primarily responsible for the appearance of low-energy intense absorption band of **1**. Fig. 4 depicts the HOMO and

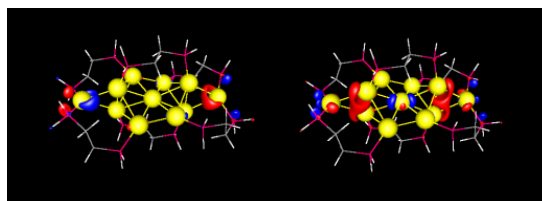


Fig. 4 LUMO (left) and HOMO (right) of $[\text{Au}_{11}(\text{H}_2\text{P}(\text{CH}_2)_2\text{PH}_2)_6]^{3+}$ (**1'**).

the LUMO of **1'**. Both orbitals are located near the triangular Au₃ units situated at both edges of the Au₁₁ entity. The LUMO is found near the exo gold atoms, whereas the HOMO is located on the shared edges of the Au₉ core and Au₃ triangles. Thus, the intense visible absorption band of **1** is mainly due to the core-to-exo intermetal transition.

In conclusion, we have determined the single-crystal structure and the optical property of a novel Au₁₁ cluster (**1**), providing experimental evidence that the attachment of extra metal atom(s) to the gold core moiety results in the generation of the unique electronic structure. Theoretical studies clearly indicate that the characteristic visible absorption is due to the HOMO–LUMO transition associated with the exo gold atoms attached to the metallic core. In contrast to conventional “core-only” clusters, which are generally brown in colour, the [core+two] clusters exhibit unique colours and thus may be potential chromogenic modules. It should be possible to tune their optical properties (colour) by varying the exo metal atoms. Developing a method for the addition reaction of non-gold atoms to core-only gold clusters for the rational design of “alloyed” [core+two] clusters is worthy of further investigation.

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Notes and references

‡ Crystallographic data for **1**-(SbF₆)₃·5EtOH: C₁₆₆H₁₇₄Au₁₁F₁₈O₅P₁₂Sb₃, *M* = 5494.57, monoclinic, *a* = 18.066(2) Å, *b* = 27.709(4) Å, *c* = 38.450(5) Å, *α* = 90.00°, *β* = 102.908(2)°, *γ* = 90.00°, *V* = 18762(4) Å³, *T* = 90 K, space group *C2/c*, *Z* = 4, 49426 reflections measured, 19177 independent reflections (*R*_{int} = 0.0629). The final *R*_i value was 0.0571 (*I* > 2σ(*I*)). The final *wR*(*F*²) values were 0.1491 (*I* > 2σ(*I*)). The final *R*_i value was 0.0996 (all data). The final *wR*(*F*²) value was 0.1794 (all data).

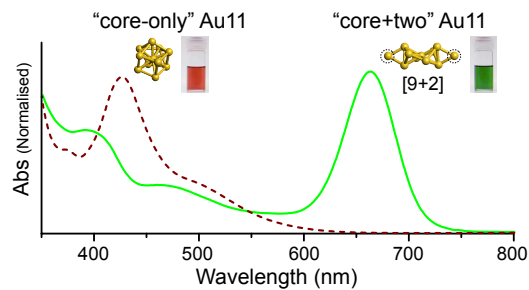
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5

A novel Au₁₁ cluster having a “core+two” ([Au₉+2Au]) geometric structure showed an evidently different absorption spectrum from that of the “core-only” isomer.
10 The role of the exo gold atoms was investigated theoretically.