Electronic Supplementary Information

Unique [core+two] structure and optical property of dodeca-ligated undecagold cluster: Critical contribution of the exo gold atoms to the electronic structure

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I. Experimental Procedures

A. Synthesis of $[Au_{11}(Ph_2P(CH_2)_2PPh_2)_6](SbF_6)_3$ (1-$(SbF_6)_3$)

To an ethanolic solution (75 mL) of $Au_2(Ph_2P(CH_2)_2PPh_2)Cl_2$ (172.7 mg, 200 μmol) was added an ethanolic solution (5 mL) of $NaBH_4$ (15.1 mg, 400 μmol), and the mixture was stirred at 0 °C. After 1 h, $NaSbF_6$ (excess) was added to the reaction mixture, which was then mixed with acetone (25 mL) / ethanol (100 mL). The resulting precipitate collected by filtration was washed with ethanol to give **1**-$(SbF_6)_3$ as a dark green solid (32.1 mg, 17%). Crystals suitable for X-ray analysis were grown from ethanol/dichloromethane (1:1). Elemental analysis: calcd (%) for **1**-$(SbF_6)_3$ ($C_{156}H_{144}Au_{11}F_{18}P_{12}Sb_3$): C 35.59, H 2.76; found: C 35.46, H 2.99; no nitrogen and chloride were found.

B. Measurements

Optical absorption spectra were recorded using a JASCO V-670 double-beam spectrometer and ESI mass spectrum was recorded on a Bruker micrOTOF-HS. ^{31}P NMR spectrum was collected at ambient temperature on a JEOL EX-400 NMR spectrometer. Chemical shifts (in ppm) were referenced to triphenylphosphine (external standard, $\delta = -4.74$). Single crystal data was collected on a Bruker SMART Apex II CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The crystal structure was solved by direct methods (SHELXS-97)[1] and refined by full-matrix least-squares methods on F^2 (SHELXL-97)[2] with APEX II software. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and refined isotropically.

II. Computational Details

All the calculations have been performed at density functional theory (DFT) level with TURBOMOLE package.[3] Geometry optimizations and vibrational frequency analyses have been computed at BP86[4,5] / double-ζ plus polarization (def-SVP)[6] level. The resolution of the identity (RI) approximation of the coulomb interaction[7] was used for speeding up. Single-point ground-state calculations were performed at the B3LYP level[8,9] with basis sets of triple-ζ valence plus polarization quality (def2-TZVP; for Au) and split valence plus polarization quality (def2-SVP; for the other elements).[10] The same exchange-correlation functional and basis sets were adopted for the subsequent calculations of electronic excitation spectra using the time-dependent (TD) DFT method. In all calculations, default 60-electron relativistic effective core potentials (ECP)[11] were employed for the Au atom.

Crystallographically determined geometric structures of gold clusters after replacement of phenyl groups with hydrogen atoms were used for initial structures of geometry optimization calculations. The fully optimized structures, which were checked to be local minima by frequency calculations, adopted the C_2 (**1’**) and C_1 (**2’**) symmetry point groups, respectively. The ground and excited state calculations of **1’** was performed considering the symmetries. Unconstrained optimizations were also performed to check that the symmetry constraints did not introduce any inconsistencies.

III. Results

A. ESI mass spectrum

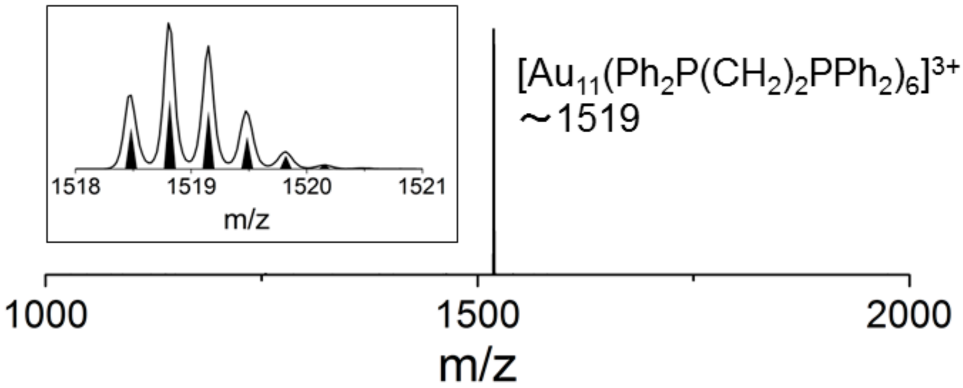

Fig. S1 Positive-ion ESI mass spectrum of **1**-$(SbF_6)_3$. The inset shows a comparison of the experimental data with the calculated isotope pattern.

B. ^{31}P NMR spectrum

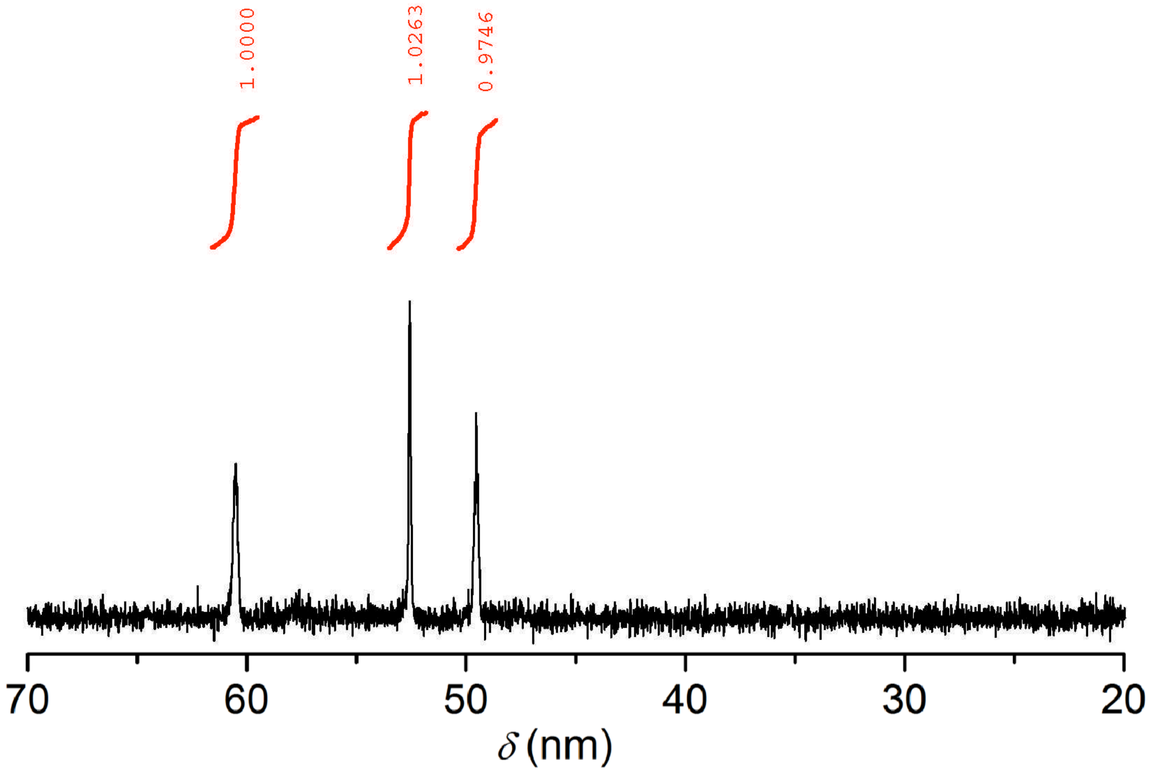

Fig. S2 Proton-decoupled ^{31}P NMR spectrum of **1**-$(SbF_6)_3$ (CD_2Cl_2) at room temperature.

C. ORTEP drawing

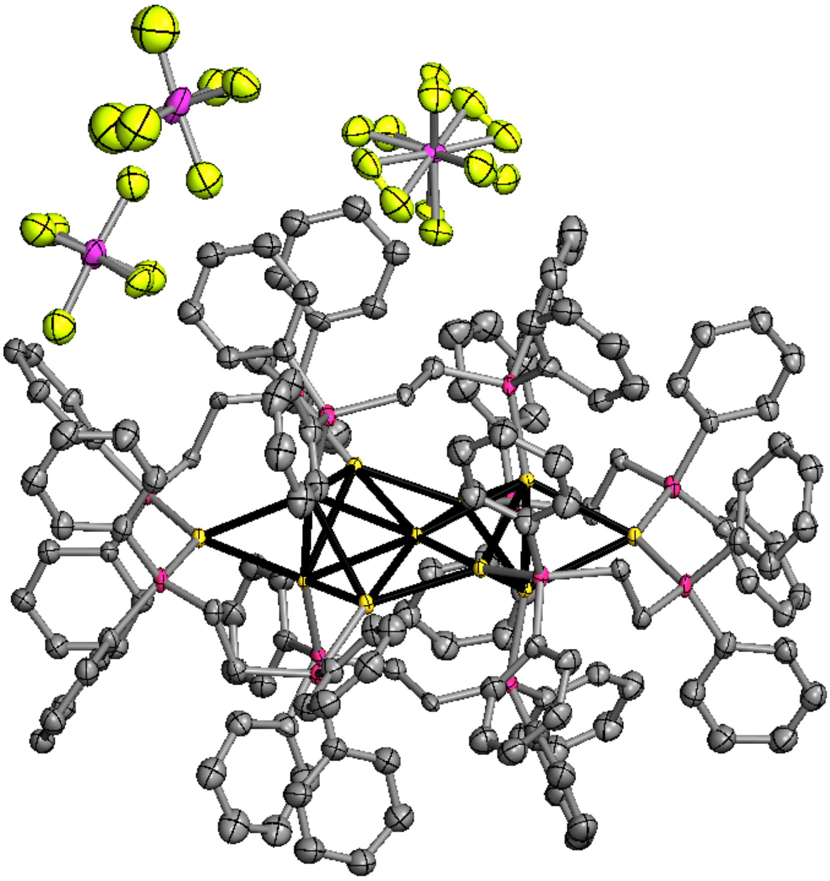

Fig. S3 ORTEP drawing of **1**-$(SbF_6)_3$. Thermal ellipsoids are drawn at the 50% probability level. For clarity, hydrogen atoms are omitted.

D. Crystal Data

Table S1. Crystal data and structure refinement for **1**-$(SbF_6)_3 \cdot 5EtOH$.

Empirical formula	$C_{166}H_{174}Au_{11}F_{18}O_5P_{12}Sb_3$	
Formula weight	5494.57	
Temperature	90 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C2/c*	
Unit cell dimensions	a = 18.066(2) Å	α = 90°
	b = 27.709(4) Å	β = 102.908(2)°
	c = 38.450(5) Å	γ = 90°
Volume	18762(4) $Å^3$	
Z	4	
Density (calculated)	1.945 Mg/m^3	
Absorption coefficient	9.155 mm^{-1}	
F(000)	10296	
Crystal size	0.14 x 0.24 x 0.24 mm^3	
Theta range for data collection	1.09 to 26.37°	
Index ranges	$-22 \le h \le 21, -34 \le k \le 18, -48 \le l \le 41$	
Reflections collected	49426	
Independent reflections	19177 [*R*(int) = 0.0629]	
Reflections with $I > 2\sigma(I)$	13077	
Completeness to theta = 26.37°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	0.3605 and 0.2173	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	19177 / 1311 / 1128	
Goodness-of-fit on F^2	1.152	
Final *R* indices $[I > 2\sigma(I)]$	$R_1 = 0.0571, wR_2 = 0.1491$	
R indices (all data)	$R_1 = 0.0996, wR_2 = 0.1794$	
Largest diff. peak and hole	3.510 and -4.562 $eÅ^{-3}$	

E. DFT results

Table S2. Kohn-Sham orbitals, energies, and atomic orbital contributions of $[Au_{11}(H_2P(CH_2)_2PH_2)_6]^{3+}$ (**1'**).

MO	Orbital index	Orbital energy (eV) / Relative energy (eV)	% Au (*sp*)	% Au (*d*)	% P (*p*)
LUMO+9	133a	-6.60 / 4.56	49	4	14
LUMO+8	132a	-6.78 / 4.38	58	4	17
LUMO+7	130b	-7.39 / 3.77	76	4	9
LUMO+6	129b	-7.42 / 3.74	65	2	12
LUMO+5	131a	-7.46 / 3.70	66	2	13
LUMO+4	130a	-7.66 / 3.50	66	5	14
LUMO+3	129a	-7.85 / 3.31	74	1	13
LUMO+2	128b	-7.87 / 3.29	71	4	13
LUMO+1	127b	-7.97 / 3.19	71	3	14
LUMO	126b	-8.74 / 2.42	71	4	14
HOMO	128a	-11.16 / 0.00	68	10	12
HOMO-1	127a	-11.58 / -0.42	59	11	18
HOMO-2	125b	-11.85 / -0.69	37	26	23
HOMO-3	126a	-12.71 / -1.56	12	64	15
HOMO-4	124b	-12.78 / -1.62	13	63	14
HOMO-5	125a	-12.80 / -1.64	21	40	27
HOMO-6	123b	-12.91 / -1.76	13	50	24
HOMO-7	122b	-13.12 / -1.96	18	59	14
HOMO-8	124a	-13.28 / -2.12	8	51	25
HOMO-9	123a	-13.30 / -2.14	19	59	15
HOMO-10	121b	-13.32 / -2.16	11	56	20

Table S3. Excited states, energies, oscillator strengths, and primary orbital-orbital transitions of $[\mathrm{Au_{11}(H_2P(CH_2)_2PH_2)_6}]^{3+}$ (**1'**).

Excitation index	Energy (eV) / Wavelength (nm)	Oscillator strength	Dominant transition	Nature of transition
1	2.20 / 564	0.5917	128a→126b	HOMO→LUMO
2	2.24 / 554	0.0003	127a→126b	HOMO-1→LUMO
3	2.58 / 480	0.0003	128a→127b	HOMO→LUMO+1
4	2.68 / 463	0.0010	128a→127b	HOMO→LUMO+1
5	2.78 / 446	0.0226	128a→129a	HOMO→LUMO+3
6	3.03 / 409	0.0636	127a→127b, 128b	HOMO-1→LUMO+1, LUMO+2
7	3.10 / 400	0.1382	127a→128b, 127b	HOMO-1→LUMO+2, LUMO+1
8	3.12 / 396	0.0076	128a→131a	HOMO→LUMO+5
9	3.15 / 394	0.0114	128a→129b	HOMO→LUMO+6
10	3.18 / 389	0.0029	128a→130b	HOMO→LUMO+7
11	323 / 383	0.0004	125b→127b	HOMO-2→LUMO+1
			127a→130a	HOMO-1→LUMO+4
12	3.28 / 378	0.0070	126a→126b	HOMO-3→LUMO
13	3.34 / 372	0.0010	125b→128b	HOMO-2→LUMO+2
14	3.36 / 369	0.0351	124b→126b	HOMO-4→LUMO
15	3.41 / 364	0.0008	125b→129a	HOMO-2→LUMO+3
16	3.41 / 363	0.0376	125a→126b	HOMO-5→LUMO
17	3.54 / 350	0.1949	127a→130a	HOMO-1→LUMO+4
			125b→127b	HOMO-2→LUMO+1
18	3.55 / 349	0.0117	127a→130b	HOMO-1→LUMO+7
19	3.60 / 344	0.0017	127a→129b	HOMO-1→LUMO+6
20	3.64 / 340	0.2844	125b→130a	HOMO-2→LUMO+4
21	3.72 / 333	0.0349	122b→126b	HOMO-7→LUMO
22	3.85 / 322	0.0041	125b→131a	HOMO-2→LUMO+5
23	3.89 / 319	0.0005	123a→126b	HOMO-9→LUMO
24	3.89 / 319	0.0160	125b→129b	HOMO-2→LUMO+6
25	3.93 / 316	0.0015	124a→126b	HOMO-8→LUMO
26	3.96 / 313	0.0092	121b→126b	HOMO-10→LUMO
27	4.00 / 310	0.0047	128a→133a	HOMO→LUMO+9
28	4.03 / 308	0.0001	126a→127b	HOMO-3→LUMO+1

Table S4. Kohn-Sham orbitals, energies, and atomic orbital contributions of $[Au_{11}(H_2P(CH_2)_3PH_2)_5]^{2+}$ (**2'**).

MO	Orbital index	Orbital energy (eV) / Relative energy (eV)	% Au (*sp*)	% Au (*d*)	% P (*p*)
LUMO+7	256a	-7.00 / 4.55	66	0	18
LUMO+6	255a	-7.19 / 4.35	66	1	17
LUMO+5	254a	-7.37 / 4.18	70	2	15
LUMO+4	253a	-8.03 / 3.52	67	6	13
LUMO+3	252a	-8.19 / 3.35	70	5	11
LUMO+2	251a	-8.27 / 3.28	73	5	11
LUMO+1	250a	-8.31 / 3.24	75	4	10
LUMO	249a	-8.37 / 3.18	73	5	10
HOMO	248a	-11.55 / 0.00	57	10	19
HOMO-1	247a	-11.71 / -0.16	54	15	19
HOMO-2	246a	-11.94 / -0.40	55	13	19
HOMO-3	245a	-12.75 / -1.20	12	54	22
HOMO-4	244a	-12.97 / -1.43	17	59	15
HOMO-5	243a	-13.02 / -1.48	20	60	12
HOMO-6	242a	-13.12 / -1.57	21	61	12
HOMO-7	241a	-13.15 / -1.61	20	61	12

Table S5. Excited states, energies, oscillator strengths, and primary orbital-orbital transitions of $[Au_{11}(H_2P(CH_2)_3PH_2)_5]^{2+}$ (**2'**).

Excitation index	Energy (eV) / Wavelength (nm)	Oscillator strength	Dominant transition	Nature of transition
1	2.52 / 491	0.0076	248a→249a	HOMO→LUMO
2	2.59 / 479	0.0079	248a→250a	HOMO→LUMO+1
3	2.60 / 478	0.0016	248a→251a	HOMO→LUMO+2
4	2.65 / 467	0.0056	247a→249a	HOMO-1→LUMO
5	2.69 / 462	0.0079	248a→252a	HOMO→LUMO+3
6	2.74 / 452	0.0117	247a→250a	HOMO-1→LUMO+1
7	2.80 / 443	0.0132	247a→251a	HOMO-1→LUMO+2
8	2.85 / 435	0.0078	248a→253a 246a→249a 247a→252a	HOMO→LUMO+4 HOMO-2→LUMO HOMO-1→LUMO+3
9	2.86 / 433	0.0158	247a→252a	HOMO-1→LUMO+3
10	2.96 / 418	0.0107	246a→250a, 252a	HOMO-2→LUMO+1, LUMO+3
11	2.99 / 414	0.0022	246a→251a 247a→253a	HOMO-2→LUMO+2 HOMO-1→LUMO+4
12	3.09 / 402	0.1623	248a→253a 246a→249a	HOMO→LUMO+4 HOMO-2→LUMO
13	3.20 / 388	0.1049	246a→253a	HOMO-2→LUMO+4
14	3.24 / 383	0.1966	246a→252a 247a→253a	HOMO-2→LUMO+3 HOMO-1→LUMO+4
15	3.26 / 380	0.1257	246a→253a	HOMO-2→LUMO+4
16	3.55 / 349	0.0187	248a→254a	HOMO→LUMO+5
17	3.69 / 336	0.0042	245a→249a 248a→255a 247a→254a	HOMO-3→LUMO HOMO→LUMO+6 HOMO-1→LUMO+5
18	3.70 / 335	0.0029	247a→254a	HOMO-1→LUMO+5
19	3.74 / 331	0.0228	248a→255a 245a→250a	HOMO→LUMO+6 HOMO-3→LUMO+1
20	3.78 / 328	0.0275	245a→251a, 250a, 249a	HOMO-3→LUMO+2, LUMO+1, LUMO
21	3.79 / 327	0.0358	245a→251a, 250a	HOMO-3→LUMO+2, LUMO+1
22	3.87 / 321	0.0030	244a→249a	HOMO-4→LUMO
23	3.88 / 320	0.0135	247a→255a	HOMO-1→LUMO+6
24	3.92 / 316	0.0311	245a→252a 246a→254a	HOMO-3→LUMO+3 HOMO-2→LUMO+5
25	3.93 / 315	0.0192	246a→254a 248a→256a	HOMO-2→LUMO+5 HOMO→LUMO+7
26	3.94 / 315	0.0156	245a→252a 248a→256a	HOMO-3→LUMO+3 HOMO→LUMO+7
27	3.98 / 312	0.0051	244a→250a 243a→250a	HOMO-4→LUMO+1 HOMO-5→LUMO+1
28	3.98 / 311	0.0257	243a→249a	HOMO-5→LUMO
29	4.01 / 309	0.0045	244a→251a 243a→250a	HOMO-4→LUMO+2 HOMO-5→LUMO+1
30	4.03 / 307	0.0150	245a→253a	HOMO-3→LUMO+4
31	4.05 / 306	0.0160	244a→251a	HOMO-4→LUMO+2
32	4.05 / 306	0.0038	243a→251a	HOMO-5→LUMO+2
33	4.06 / 305	0.0433	242a→249a	HOMO-6→LUMO
34	4.07 / 304	0.0129	244a→252a	HOMO-4→LUMO+3
35	4.10 / 302	0.0396	241a→249a	HOMO-7→LUMO
36	4.11 / 302	0.0128	247a→256a	HOMO-1→LUMO+7
37	4.13 / 301	0.0060	246a→255a	HOMO-2→LUMO+6
38	4.13 / 300	0.0072	242a→250a 246a→255a	HOMO-6→LUMO+1 HOMO-2→LUMO+6

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