Electronic Supplementary Material (ESI) for Nanoscale.
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$[Ag_{15}(N\text{-triphos})_4(Cl_4)](NO_3)_3$: A Stable Ag-P Superatom with Eight-Electrons (N-triphos = Tris((diphenylphosphino)methyl)amine)

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Experiment Section

All reagents were purchased from commercial sources and used without further purification. Ligand N-triphos was prepared according to the reference (P. W. Miller and A. J. P. White, *J. Organomet. Chem*. 2010, *695*, 1138–1145).

Synthesis of $[Ag_{15}(N\text{-triphos})_4(Cl_4)](NO_3)_3{\cdot}8H_2O$:
30mg (0.05mmol) N,N,N-tris(diphenylphosphinomethyl)amine in 3.0 mL MeOH was added to the solution of 60 mg (0.35mmol) $AgNO_3$ in 0.5 mL of deionized water, and the resulting reaction solution was stirred at room temperature using a magnetic stirrer. After 20 minutes, a fresh solution of 20 mg (0.53mmol) of $NaBH_4$ in 6.0 mL of MeOH was added into this reaction solution. And then the resulting reaction mixture was stirred continuously for over 20h at room temperature. After that, the solvents were removed by rotary evaporation at room temperature. The dried product was extracted by 7 mL of $CHCl_3$ and then the extracted mixture was centrifuged for 1min at 6000r/min. The dark red supernatant was filtrated and the filtration was diffused slowly by ether through the vapor phase. Dark sheet crystals were afforded in one week. Yield: 11.35 mg，10.8% based on Ag^+ ion. Elemental analysis calcd (%) for $C_{156}H_{160}Ag_{15}Cl_4N_7O_{17}P_{12}$: C 41.30, H 3.55, N 2.16; found: C 41.58, H 3.91, N 2.42.

Note: Following the aforementioned procedure, the compound **1** can also be obtained by using $NaBD_4$, CD_3OD and D_2O instead of $NaBH_4$, CH_3OH and H_2O, respectively.

Physical measurements
IR spectra were recorded as KBr pellets on a Perkin-Elmer FT-IR spectrometer in the range 4000−450 cm^{-1}. Elemental analyses were performed with a Carlo ERBA 1106 analyzer. Powder X-ray diffraction (PXRD) data were collected on a Rigaku D/Max 2500 diffractometer (CuKα, λ = 1.5418 Å). UV-vis spectra were recorded using a Cary series UV-Vis spectrometer. High resolution mass spectra were recorded using a Thermo Exactive in positive ion mode, the capillary temperature: 350℃; the capillary voltage: 57.5 V; the tube lens voltage: 160V; the skimmer voltage: 20 V. X-ray Photoelectron Spectroscopy (XPS) was carried out using a monochromatic Al Kα (1486.69 eV) X-ray source operated on ESCALAB 250Xi, and the spectra were calibrated using the C 1s peak at 284.5 eV.

Crystal data and experimental details for **1** were given in Table S1. X-ray Diffraction data of complex **1** were obtained at 1W1A, Beijing Synchrotron Radiation Facility (λ = 0.72 Å) at 107 K. All calculations were performed with Olex2 crystallographic software package. The structure was solved by the standard direct method and refined in the anisotropic approximation. The diffraction data of **1** was not enough good since the crystal was sheet. Therefore all phenyl rings on N-triphos were not standard and had to been fixed theoretically. Counter anions NO_3^- and solvent molecules were seriously disorder and couldn't be determined directly by the structure refinement. The number of counter anion NO_3^- was determined by elemental analysis and confirmed by ESI-MS. Hydrogen atoms were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The final refinements had been carried out with SQUEEZE data. The crystal data has been deposited to the Cambridge Structural Database and the CCDC number: 1576513.

Table S1 Crystal data and structure refinement for 1

Empirical formula	$C_{156}H_{144}Ag_{15}Cl_4N_7O_9P_{12}$·xsolvent
Crystal system	orthorhombic
Space group	*C222₁* → $C222_1$
a (Å)	18.702(4)
b (Å)	36.975(7)
c (Å)	28.652(6)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	19813(7)
Z	4
ρ_{calc} (g/cm^{-3})	1.410
μ (mm^{-1})	1.669
θ range for data collection	2.469 to 25.057
Reflections collected	30936
Independent reflections	16793
Data/restraints/parameters	16793 / 1140 / 730
Goodness of fit (GOF)	1.070
Final R indices [$I > 2\sigma(I)$]	0.0973
R indices (all data)	0.1132
Largest diff. peak / hole /eÅ^{-3}	3.463/-3.608

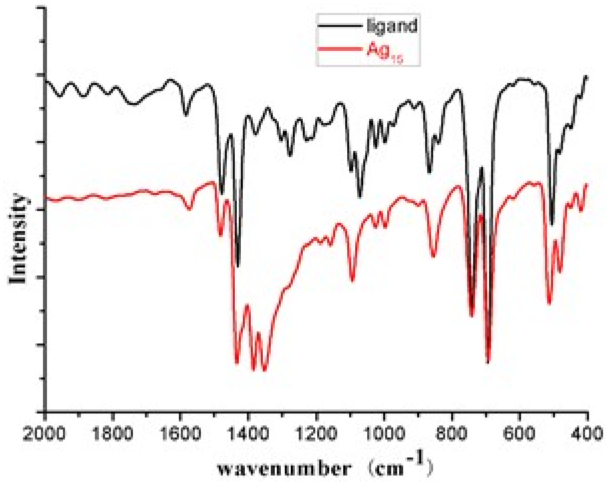

Fig. S1 IR spectra of ligand N-triphos and $[Ag_{15}(N\text{-triphos})_4(Cl_4)](NO_3)_3$.

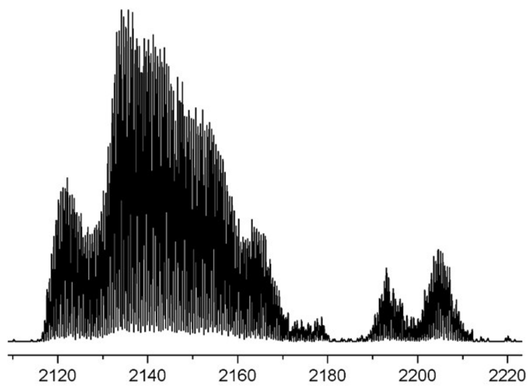

Fig. S2 Positive-ion mode ESI-MS of single crystal of $[Ag_{15}(N\text{-triphos})_4(Cl_4)](NO_3)_3$ in CH_3OH, showing some overlapped peaks at 2120~2220.

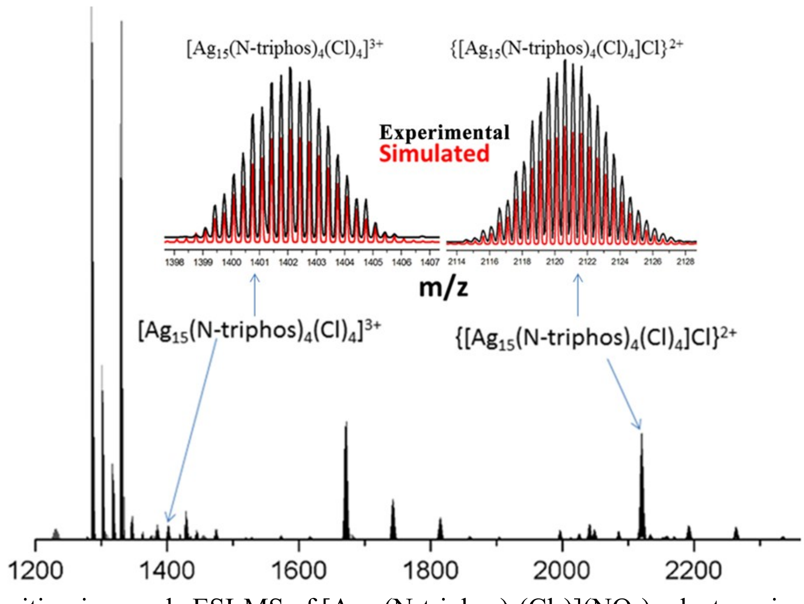

Fig. S3 Positive-ion mode ESI-MS of $[Ag_{15}(N\text{-triphos})_4(Cl_4)](NO_3)_3$ cluster mixed with the excess KCl in CH_3OH solution, showing molecular ion peaks of $[Ag_{15}(N\text{-triphos})_4(Cl)_4]^{3+}$ and $\{[Ag_{15}(N\text{-triphos})_4(Cl)_4]Cl\}^{2+}$.

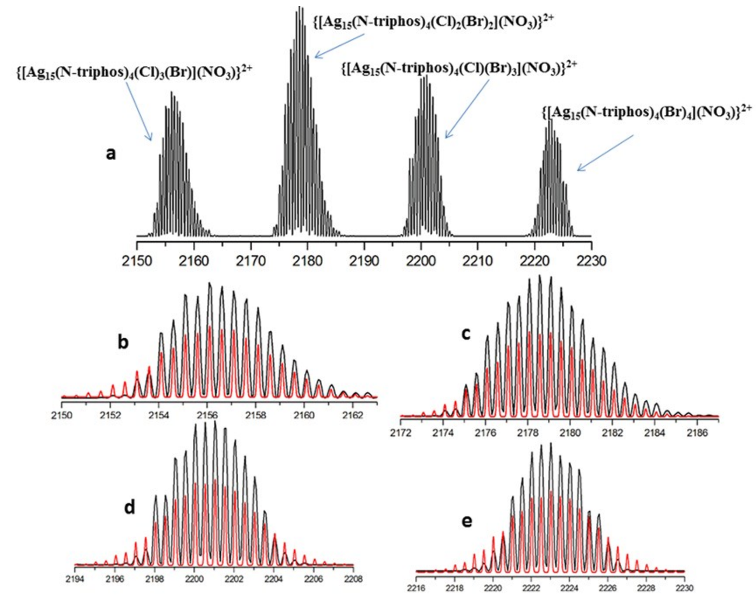

Fig. S4 (a) Positive-ion mode ESI-MS of $[Ag_{15}(N\text{-triphos})_4(Cl_4)](NO_3)_3$ cluster mixed with the excess KBr in CH_3OH solution, exhibiting anion exchange behaviors. (b-c) showing a good agreement of experimental (black) and simulated (red) mass spectra of $\{[Ag_{15}(N\text{-triphos})_4(Cl)_3(Br)](NO_3)\}^{2+}$, $\{[Ag_{15}(N\text{-triphos})_4(Cl)_2(Br)_2](NO_3)\}^{2+}$, $\{[Ag_{15}(N\text{-triphos})_4(Cl)(Br)_3](NO_3)\}^{2+}$ and $\{[Ag_{15}(N\text{-triphos})_4(Br)_4](NO_3)\}^{2+}$, respectively.

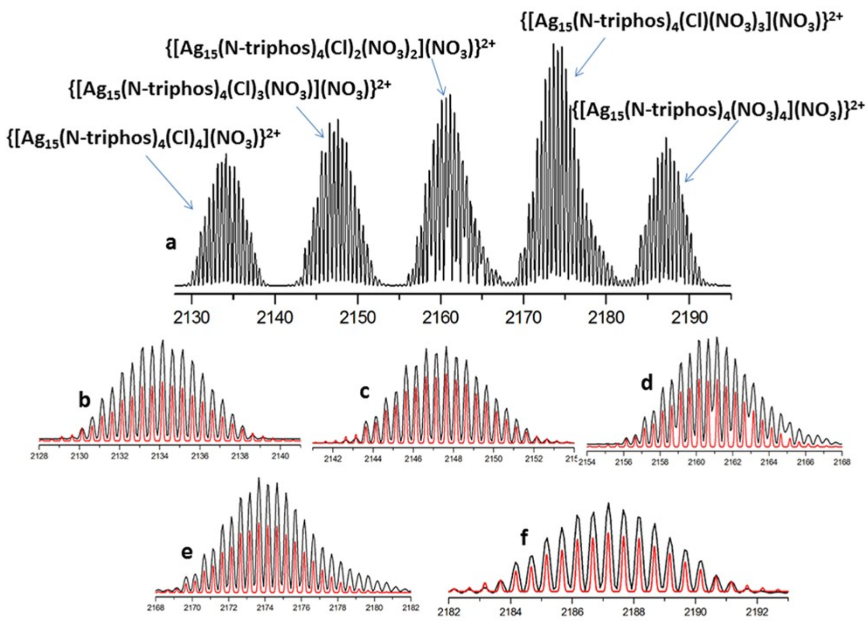

Fig. S5 (a) Positive-ion mode ESI-MS of $[Ag_{15}(N\text{-triphos})_4(Cl_4)](NO_3)_3$ cluster mixed with the excess KNO_3 in CH_3OH solution. (b-f) showing a good agreement of experimental (black) and simulated (red) mass spectra of $\{[Ag_{15}(N\text{-triphos})_4(Cl)_4](NO_3)\}^{2+}$, $\{[Ag_{15}(N\text{-triphos})_4(Cl)_3(NO_3)](NO_3)\}^{2+}$, $\{[Ag_{15}(N\text{-triphos})_4(Cl)_2(NO_3)_2](NO_3)\}^{2+}$, $\{[Ag_{15}(N\text{-triphos})_4(Cl)(NO_3)_3](NO_3)\}^{2+}$ $\{[Ag_{15}(N\text{-triphos})_4(NO_3)_4](NO_3)\}^{2+}$, respectively.

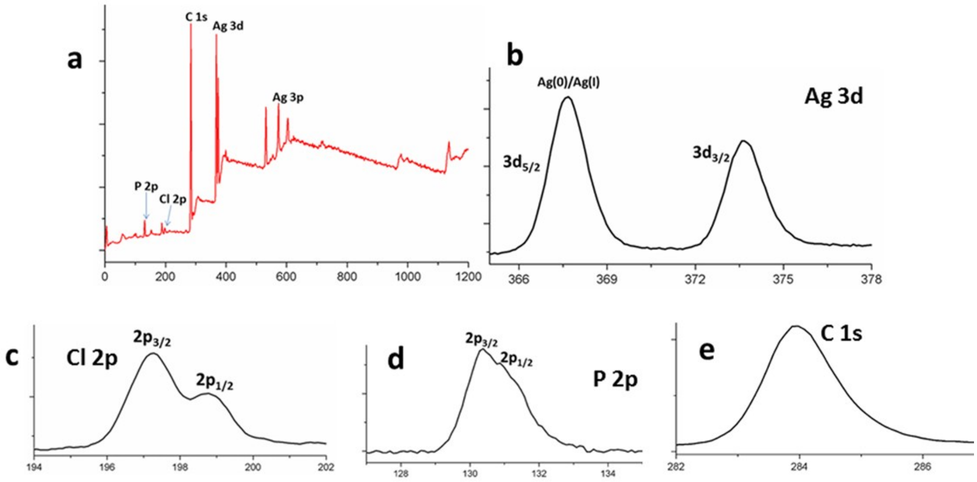

Fig. S6 XPS spectra of $[Ag_{15}(N\text{-triphos})_4(Cl_4)](NO_3)_3$ cluster. (a) Survey spectrum, showing all the expected elements (Ag, P, Cl and C). (b-e) Specific regions of Ag 3d, Cl 2p, P 2p and C 1s, respectively.

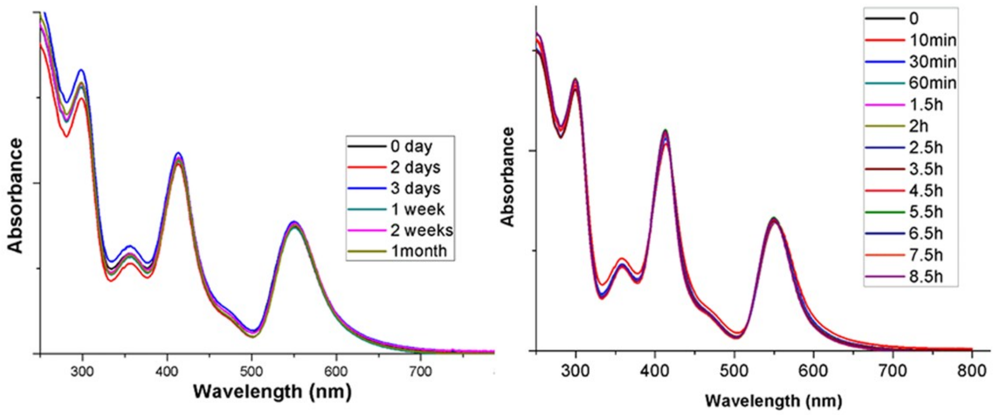

Fig. S7 UV-vis spectra of $[Ag_{15}(N\text{-triphos})_4(Cl_4)](NO_3)_3$ cluster in CH_3OH (2.5×10^{-5} mol·L^{-1}) monitored with time, checking the time-dependent ambient stability of cluster in CH_3OH in dark (a) and in natural light (b).

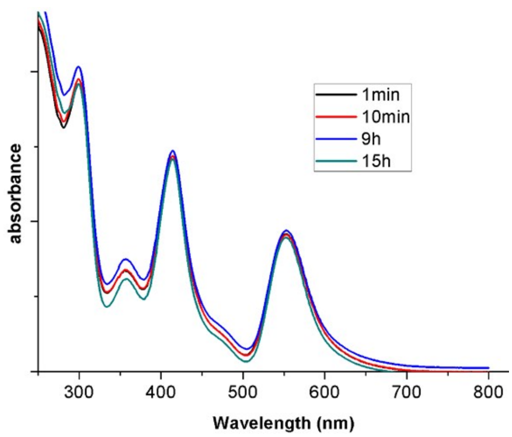

Fig. S8 UV-vis spectra of $[Ag_{15}(N\text{-triphos})_4(Cl_4)](NO_3)_3$ cluster in CH_3OH (2.5×10^{-5} mol·L^{-1}) at 50ºC in dark, monitored with time.

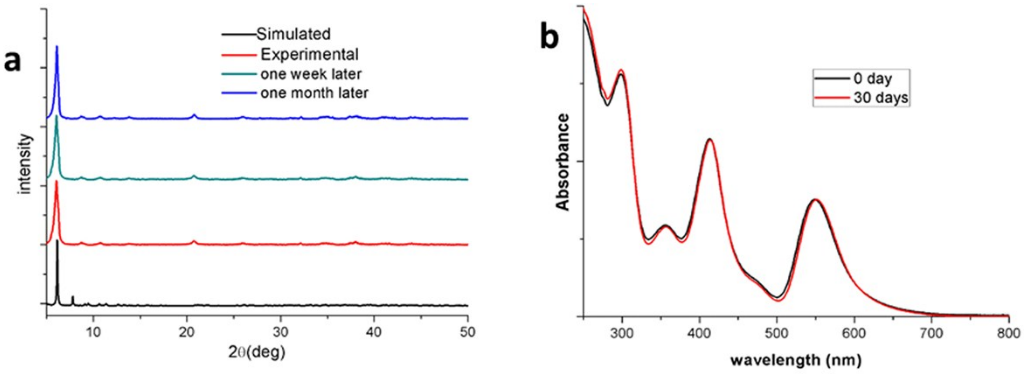

Fig. S9 Monitoring the time-dependent ambient stability of $[Ag_{15}(N\text{-triphos})_4(Cl_4)](NO_3)_3$ cluster as a solid. (a) Powder X-ray diffraction data; (b) UV-vis spectra, the solid-state cluster was dissolved in CH_3OH for recording the UV-vis spectra. Solid-state samples were stored in natural light.

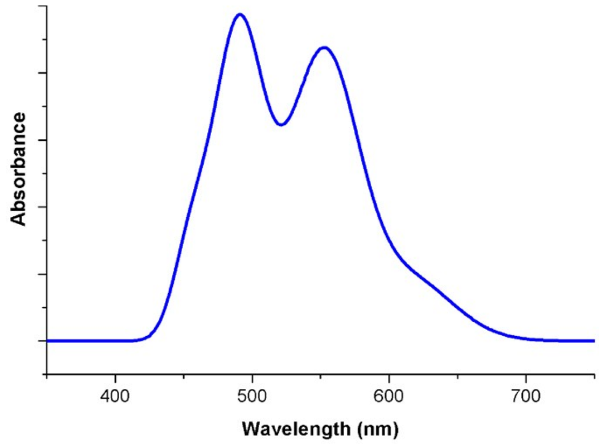

Fig. S10 the simulaton of UV-vis spectrum of 1 by TD-DFT

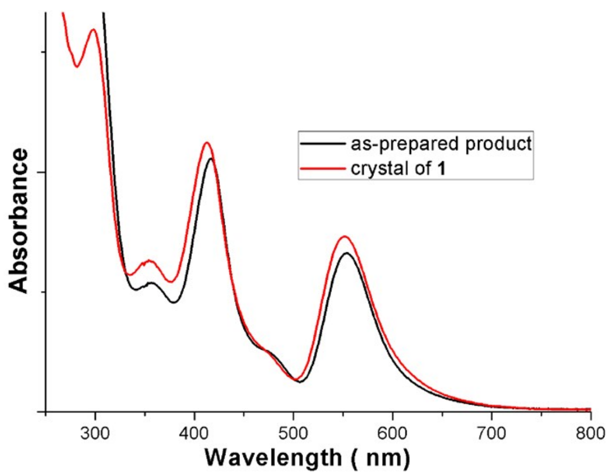

Fig. S11 UV-vis spectra of the as-prepared product and the crystal of $[Ag_{15}(N\text{-triphos})_4(Cl_4)](NO_3)_3$ in $CHCl_3$.

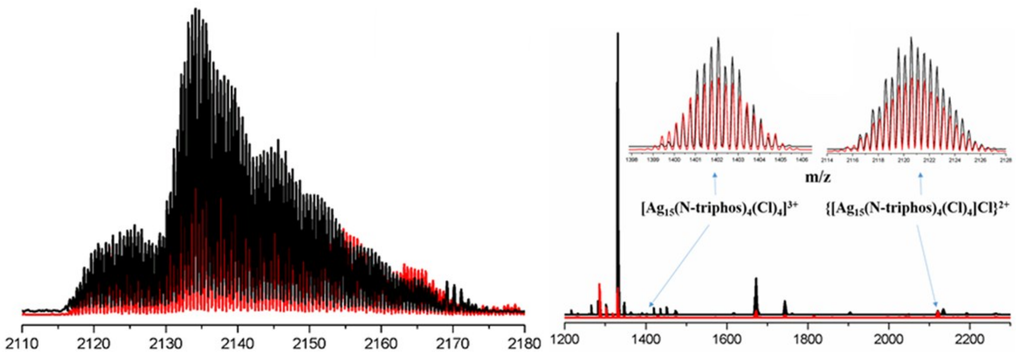

Fig. S12 the Positive-ion mode ESI-MS spectra of nanocluster **1** by using $[BH_4]^-$ (red) and $[BD_4]^-$ (black). (a) showing an almost identical ESI-MS spectra of **1** in methanol at 2110~2180. (b) showing an almost identical ESI-MS spectra of **1** at 1200~2200 with the excess of KCl in methanol, inset: the ESI-MS spectra of $[Ag_{15}(N\text{-triphos})_4(Cl_4)]^{3+}$ and $\{[Ag_{15}(N\text{-triphos})_4(Cl_4)]Cl\}^{2+}$.

Computational Details

All the calculations were performed via Gaussian 16 program[1]. In order to reduce the expense of computation, the structure of $[Ag_{15}(N\text{-triphos})_4(Cl)_4]^{3+}$ is simplified. The phenyl group was replaced by hydrogen atom. Density functional theory (DFT) calculation at the hybrid Becke, three-parameter Lee-Yang (B3LYP) level[2] was carried out to optimize the structure of the model complex. The def2-SVP basis set[3] was selected as a compromise of reasonable accuracy and computational effort. The UV−visible absorption spectra of the complexes were investigated using TD-DFT calculations at TPSSh[4]/def2-TZVP level based on the simplified model complex.

References

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Cartesian coordinates of the optimized geometry

Ag	0.00018000	-0.21704500	-0.26586100
Ag	2.12406300	-1.17716700	-1.59529000
Ag	1.72135400	1.98886100	-0.74798100
Ag	-1.23253700	2.01471200	-1.13781700
Ag	1.66870300	-2.00974400	1.09354100
Ag	0.02842600	-3.05289800	-1.24721200
Ag	0.38623200	0.77225400	-3.19571700
Ag	0.03136200	3.51507300	1.06800200
Ag	3.92931300	-0.06614800	0.41030800
Cl	4.11351200	1.89377300	-1.51808400
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