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Supporting Information

Alkynyl-Protected Au_{40} Nanocluster featuring a PhC≡C–Au–P staple

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Contents

I. Physical measurements

UV-vis-NIR absorption spectra were recorded on Cary 5000. Mass spectra were recorded on Agilent Technologies ESI-TOF-MS. NMR data were recorded on a Bruker Avance II spectrometer (500MHz). ^{31}P chemical shifts were referenced to external 85% H_3PO_4. Thermogravimetric analysis (TGA) was performed on TG_209F1.

X-ray Crystallography. Intensity data of compound **1** were collected on an Agilent SuperNova Dual system (Cu Kα). Absorption corrections were applied by using the program CrysAlis (multi-scan). The structure was solved by direct methods, and non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL program. All the phenyl groups were refined using a rigid model (AFIX 66). SQUEEZE tool of PLATON was applied in the structure of **1**, due to large solvent voids.

II. Experimental Details

Materials and reagents. Ethynylbenzene (PhC≡CH, 98%), Sodium hexafluoroantimonate ($NaSbF_6$, 99%), Bis(diphenylphosphino)methane (dppm, 98%) were purchased from J&K; Silver trifluoroacetate ($AgOOCCF_3$, 98.0 %) were purchased from Strem Chemicals Inc.; Sodium borohydride ($NaBH_4$, 98%) and other reagents employed were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All reagents were used as received without further purification.

dppm($AuOOCCF_3$)$_2$

The synthesis of dppm($AuOOCCF_3$)$_2$ is entirely different from PPh_3AuX (X = SbF_6 and CF_3SO_3)[1-3]. To obtain the solution of dppm($AuOOCCF_3$)$_2$, a solution of CF_3COOAg (8.8 mg, 0.04 mmol) in 0.1 mL CH_3OH was added dropwise to the solution of Me_2SAuCl (11.8 mg, 0.04 mmol) in 3 mL CH_2Cl_2 with vigorous stirring, and the solution turned into a suspension immediately.The reaction continued for 15 min at room temperature in the dark obtaining the AgCl precipitate and a solution of $Me_2SAuOOCCF_3$ which could be stable in solution owing to the coordination ability of the CF_3COO^-. While the anions possessing weaker coordination ability of the other silver salts (eg. $AgSbF_6$, $AgNO_3$ and AgOTf) are not able to stabilize the Me_2SAu^+ solution. Then, the resulting solution was centrifuged for 3 min at 9000 r/min, and the AgCl precipitate was filtered off. The dppm (5.7 mg, 0.02 mmol) was add to the solution of $Me_2SAuOOCCF_3$ obtaining the solution of dppm($AuOOCCF_3$)$_2$. This method to synthesize the solution $LAuOOCCF_3$ is effective for phosphine ligands, especially for those phosphine ligands whose R_3PAuCl compounds are not soluble.

[Au_{40}(PhC≡C)$_{20}$(dppm)$_4$](SbF_6)$_4$

To 4 mL CH_2Cl_2 solution of dppm($AuOOCCF_3$)$_2$ (0.04 mmol), PhC≡CAu (47.7 mg, 0.16 mmol) was added. And a freshly prepared solution of $NaBH_4$ (0.76 mg in 1 mL of ethanol) was added dropwise under vigorous stirring. The solution color changed from orange to pale brown and finally to dark brown. 30 min later, $NaSbF_6$ (52 mg, 0.2 mmol) was added and the reaction continued for 24 h at room temperature in air in the dark. The mixture was evaporated to dryness to give a dark solid, which was dissolved in 1 mL CH_2Cl_2 and 1 mL CH_2Cl-CH_2Cl centrifuged for 3 min at 9000 r/min. The supernatant solution was subject to the diffusion of n-hexane to afford 3.3 mg brown-red crystals after two weeks (5.3 % yield based on Au).

Reference

(1) Wan, X.-K.; Yuan, S.-F.; Tang, Q.; Jiang, D.-e.; Wang, Q.-M., *Angew. Chem. Int. Ed.* **2015,** *54*, 5977.
(2) Wan, X.-K.; Wang, J.-Q.; Nan, Z.-A.; Wang, Q.-M., *Science Advances* **2017,** *3*.
(3) Wan, X.-K.; Xu, W. W.; Yuan, S.-F.; Gao, Y.; Zeng, X.-C.; Wang, Q.-M., *Angew. Chem. Int. Ed.* **2015,** *54*, 9683.

III. Characterization

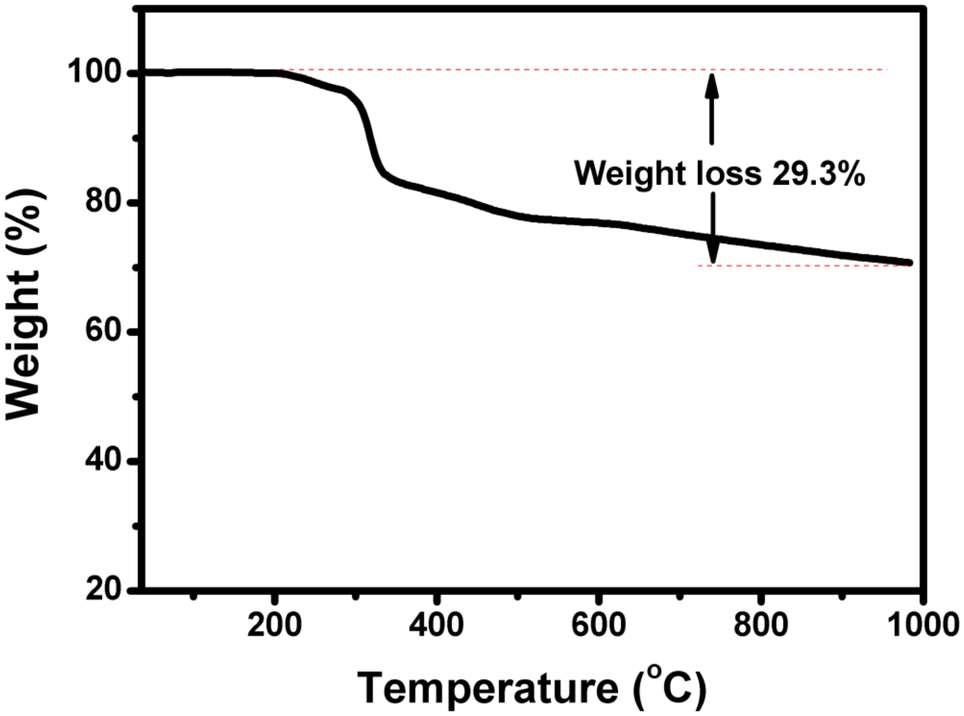

Figure S1. TGA of cluster **1**.

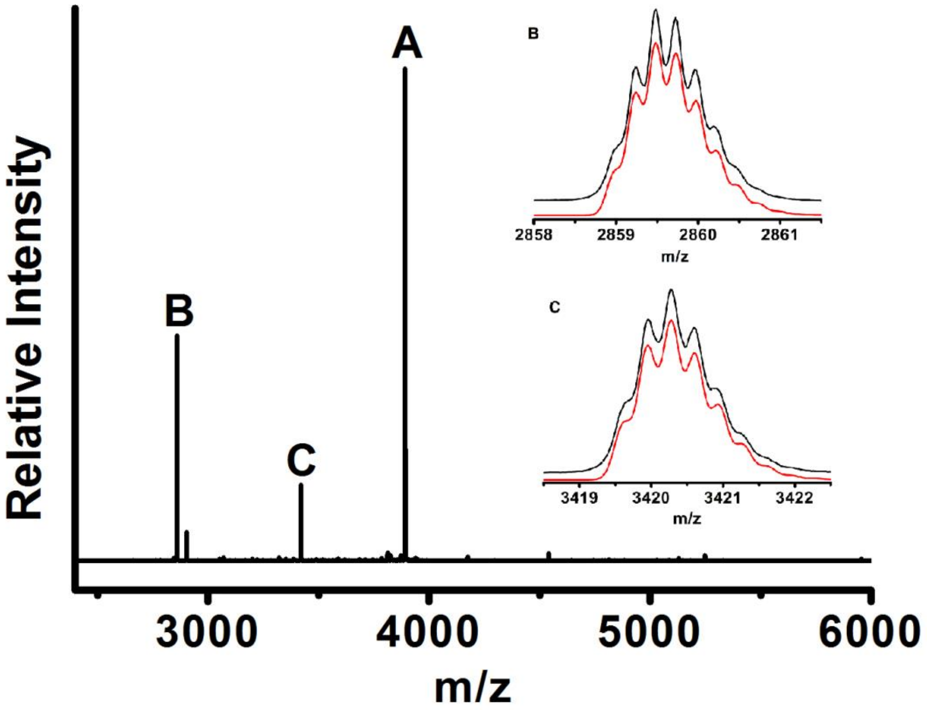

Figure S2. ESI-TOF-MS spectrum of cluster **1**. Inset: the measured (black trace) and simulated (red trace) isotopic patterns. (A) $[Au_{40}(PhC{\equiv}C)_{20}(dppm)_4SbF_6]^{3+}$; (B) $[Au_{40}(PhC{\equiv}C)_{20}(dppm)_4]^{4+}$ (C) $[Au_{37}(PhC{\equiv}C)_{18}(dppm)_3]^{3+}$.

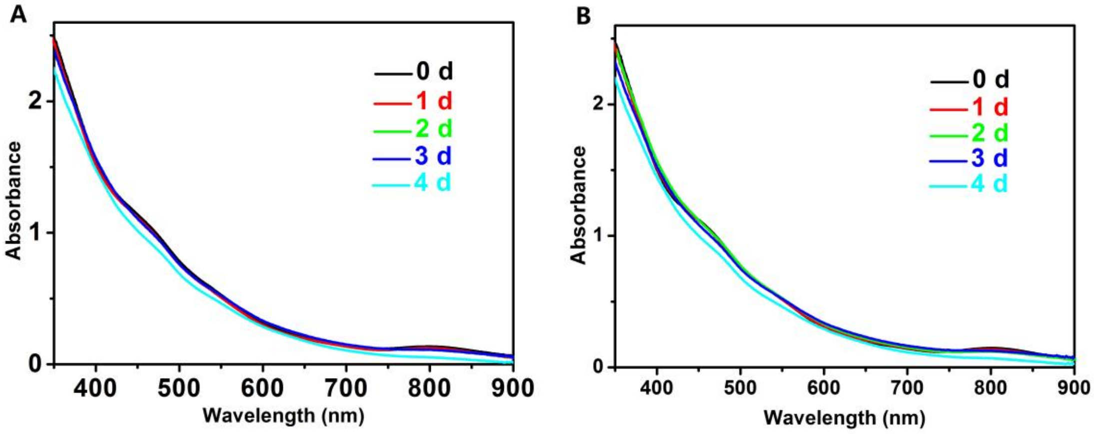

Figure S3. Time-dependent UV-Vis spectra of **1** for monitoring stability. (A) under ambient conditions in CH_2Cl_2; (B) under ambient conditions in CH_2Cl_2 in dark.

Table S1. Crystal data and structure refinement for $[\mathrm{Au_{40}(PhC{\equiv}C)_{20}(dppm)_4](SbF_6)_4}$.

Empirical formula Formula weight	$\mathrm{C_{263}H_{194}Au_{40}Cl_4F_{24}P_8Sb_4}$ 12565.39
Temperature	173.00(10) K
Wavelength	1.54184 Å
Crystal system, space group	monoclinic, *C*2/*c*
Unit cell dimensions	a = 41.9547(10) Å α = 90° b = 18.5701(3) Å β = 117.333(3)° c = 44.4220(11) Å γ = 90°
Volume	30745.3(14) $Å^3$
Z, Calculated density	4, 2.715 g/cm^3
Absorption coefficient	38.741 mm^{-1}
F(000)	22160.0
Crystal size	0.08 × 0.03 × 0.02 mm
Theta range for data collection	7.624 to 122.338
Limiting indices	$-47 \leq h \leq 47$, $-16 \leq k \leq 21$, $-45 \leq l \leq 50$
Reflections collected	74308
Independent reflections	23118 [R_{int} = 0.0969, R_{sigma} = 0.0779]
Data/restraints/parameters	23118/890/1410
Goodness-of-fit on F^2	1.057
Final R indices [I>2sigma(I)]	R_1 = 0.0927, wR_2 = 0.2476
R indices (all data)	R_1 = 0.1062, wR_2 = 0.2615
Largest diff. peak and hole	4.36/-5.56 $e.A^{-3}$