Supporting Information:

Cocrystallization-Driven Stabilization of Metastable Nanoclusters: A Case Study of Pd_1Au_9

Honglei Shen,[a,b,§] Xiao Wei,[a,b,§] Chao Xu,[a,b] Shuxin Wang,[c] Shan Jin,[a,b] Xi Kang,[a,b,*] Manzhou Zhu[a,b,*]

[a]Department of Chemistry and Centre for Atomic Engineering of Advanced Materials, Anhui Province Key Laboratory of Chemistry for Inorganic/Organic Hybrid Functionalized Materials, Anhui University, Hefei 230601, P. R. China.
[b]Key Laboratory of Structure and Functional Regulation of Hybrid Materials, Anhui University, Ministry of Education, Hefei 230601, P. R. China.
[c]College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China.

[§]H.S. and X.W. contributed equally.

*E-mails of corresponding authors: kangxi_chem@ahu.edu.cn (X.K.); zmz@ahu.edu.cn (M.Z.).

Notes: The authors declare no competing financial interest.

This Supporting Information includes:
Figs. S1-S7
Tables S1-S6

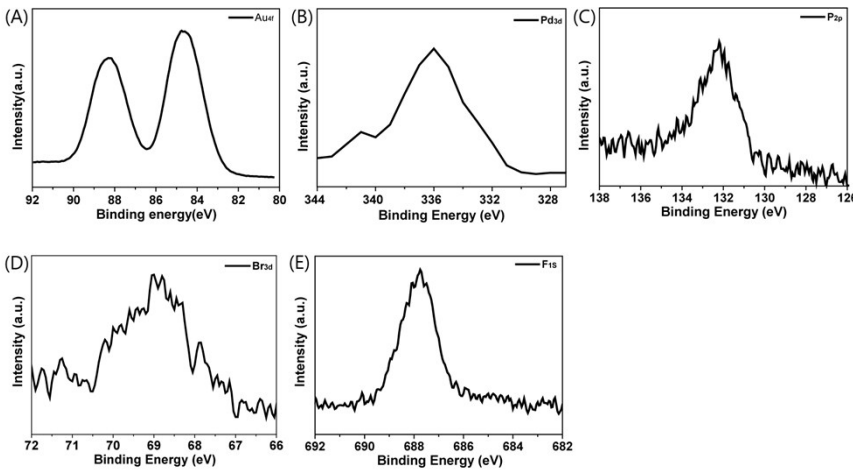

Fig. S1 XPS spectra of (A) Au4f, (B) Pd3d, (C) P2p, (D) Br3d, and (E) F1S of the $[Pd_1Au_9(TFPP)_7Br_2]^+$ nanocluster.

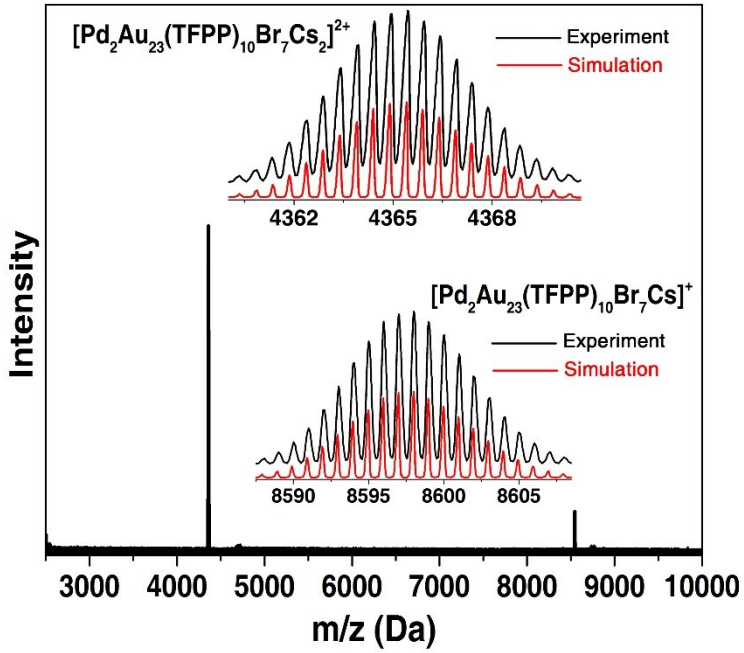

Fig. S2 ESI-MS result of the $Pd_2Au_{23}(TFPP)_{10}Br_7$ nanocluster. The experimental mass peaks excellently match the simulated isotope patterns. Insets: comparison of experiment (black trace) and simulated (red) isotopic distributions. Cs^+ ions (CH_3COOCs) are introduced in the mass detection, and the detected signals are assigned to $[Pd_2Au_{23}(TFPP)_{10}Br_7\text{-}Cs_1]^+$ and $[Pd_2Au_{23}(TFPP)_{10}Br_7\text{-}Cs_2]^{2+}$, respectively.

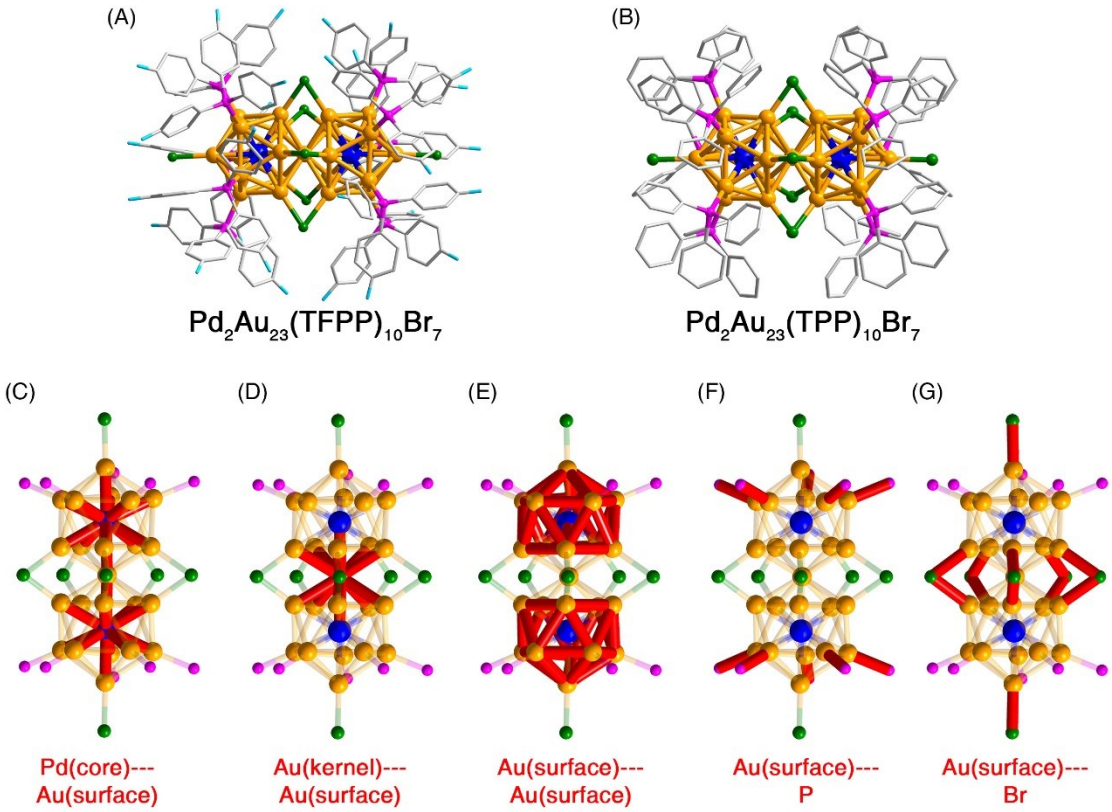

Fig. S3 Comparison of corresponding bond lengths between $Pd_2Au_{23}(TPP)_{10}Br_7$ and $Pd_2Au_{23}(TFPP)_{10}Br_7$. The only difference between $Pd_2Au_{23}(TFPP)_{10}Br_7$ and $Pd_2Au_{23}(TPP)_{10}Br_7$ are their phosphine ligands (Figure S2A,B). Figure S2C-G depicts the compared bond lengths in Pd_2Au_{23} nanoclusters. The comparisons of bond length between two Pd_2Au_{23} nanoclusters are shown in Table S1. Specifically, compared with $Pd_2Au_{23}(TFPP)_{10}Br_7$, the average Pd---Au bond length of $Pd_2Au_{23}(TPP)_{10}Br_7$ is reduced by 0.36%, and the average bond length of kernel Au---surface Au is reduced by 0.18%. On the contrary, the average Au---Br bond length of $Pd_2Au_{23}(TFPP)_{10}Br_7$ is much longer than that $Pd_2Au_{23}(TPP)_{10}Br_7$.

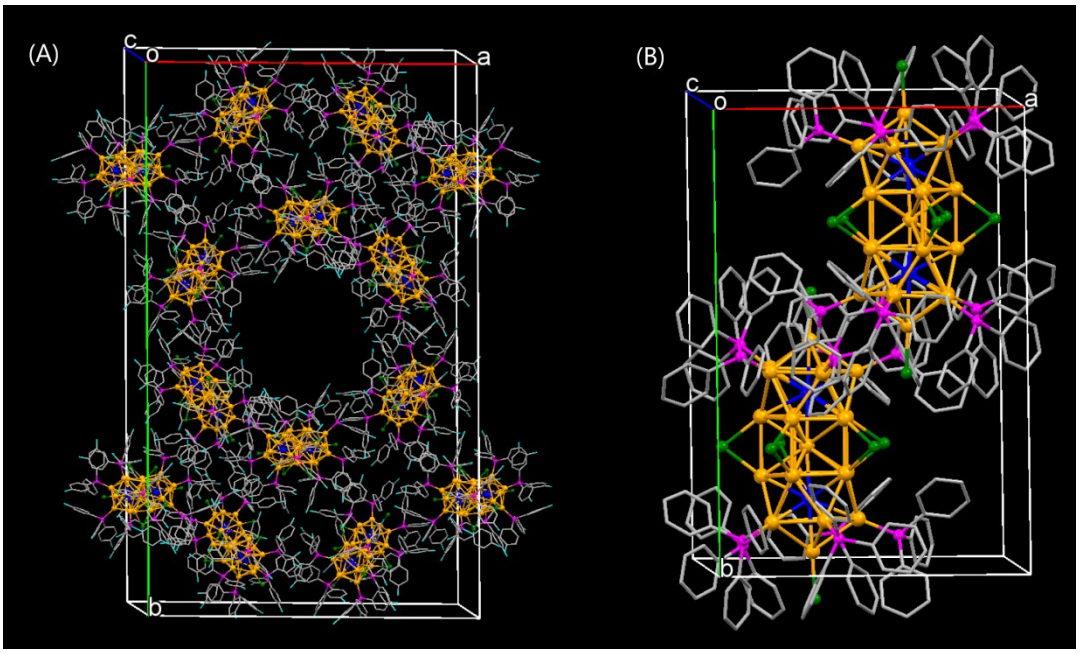

Fig. S4 Comparison of crystalline packing modes of (A) $Pd_2Au_{23}(TFPP)_{10}Br_7$ and (B) $Pd_2Au_{23}(TPP)_{10}Br_7$. The crystalline packing modes of these two Pd_2Au_{23} nanoclusters are different. The unit cell of $Pd_2Au_{23}(TFPP)_{10}Br_7$ contains more cluster molecules compare to that of $Pd_2Au_{23}(TPP)_{10}Br_7$. Color legends: orange, Au; blue, Pd; green, Br; magenta, P; gray, C; light blue, F. For clarity, all H atoms are omitted.

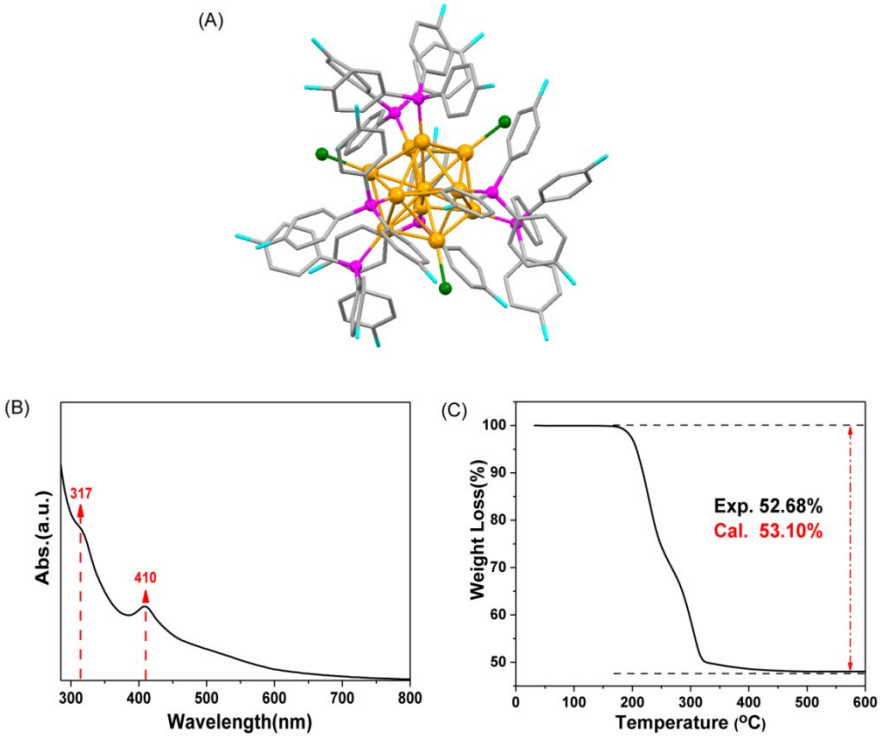

Fig. S5 Characterizations of $Au_{11}(TFPP)_7Br_3$. (A) Crystal structure of $Au_{11}(TFPP)_7Br_3$. (B) UV-vis of $Au_{11}(TFPP)_7Br_3$ (dissolved in CH_2Cl_2). (C) TGA of $Au_{11}(TFPP)_7Br_3$.

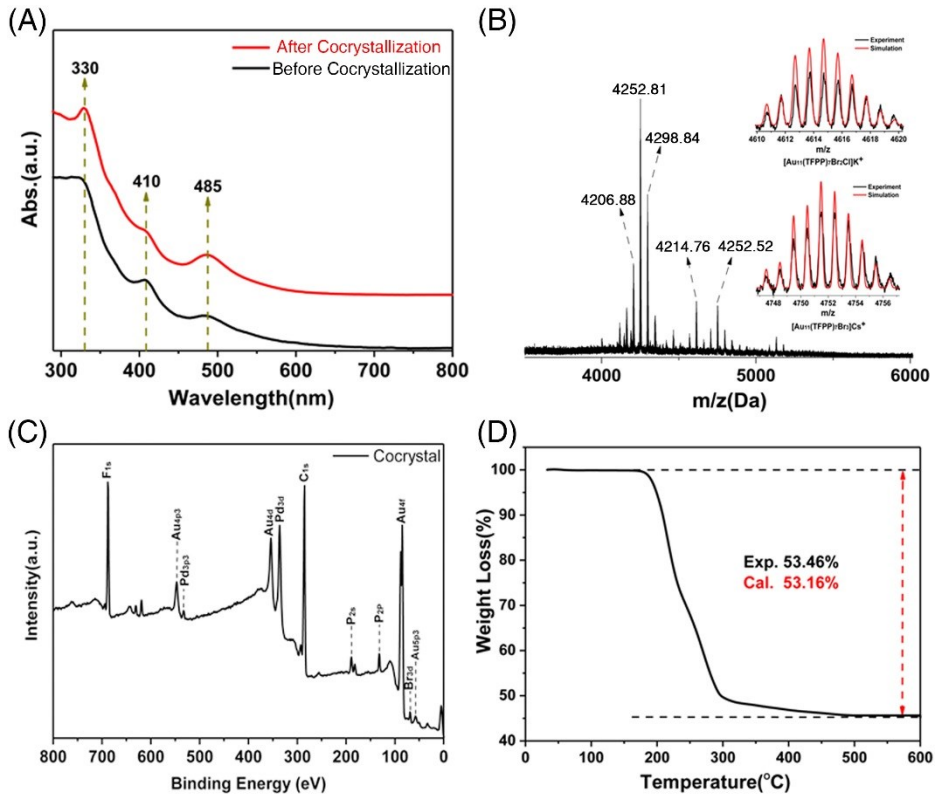

Fig. S6 Characterizations of the cocrystallized $Pd_1Au_9(TFPP)_6Br_3$@$Au_{11}(TFPP)_7Br_3$. (A) UV-vis. (B) ESI-MS. The peaks at 4206.88, 4252.81, and 4298.84 Da belong to the $[Pd_1Au_9(TFPP)_7Br_2]^+$ nanocluster, corresponding to Figure 1B. The signals at 4214.76 and 4252.52 Da are assigned to $[Au_{11}(TFPP)_7Br_2Cl_1]K^+$ and $[Au_{11}(TFPP)_7Br_3]Cs^+$, respectively. (C) XPS. (D) TGA.

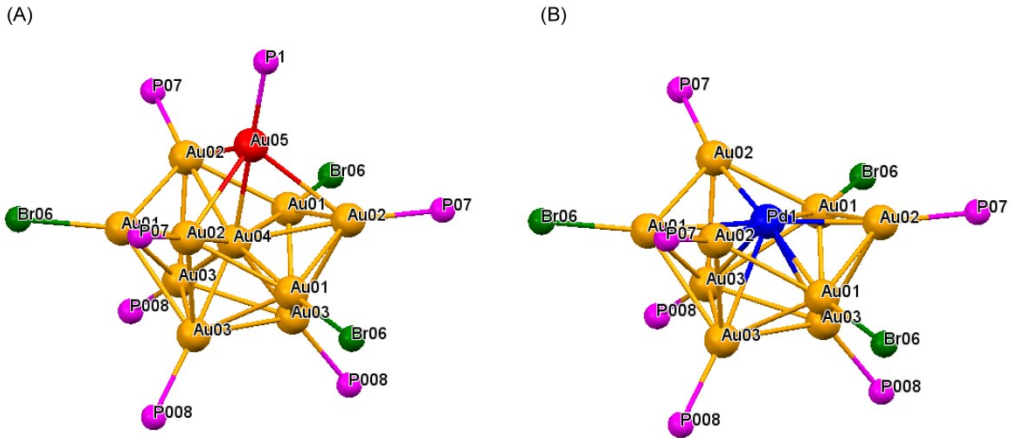

Fig. S7 Structural comparison between $Pd_1Au_9(TFPP)_6Br_3$ and $Au_{11}(TFPP)_7Br_3$. Color legends: orange and red, Au; blue, Pd; green, Br; purple, P. For clarity, all H, C and F atoms are omitted.

Table S1. Comparison of corresponding bond lengths between $Pd_2Au_{23}(TPP)_{10}Br_7$ and $Pd_2Au_{23}(TFPP)_{10}Br_7$. The corresponding bonds are highlights in Figure S2.

Cluster	Pd(core)---Au(surface)	Au(kernel)---Au(surface)	Au(surface)---Au(surface)	Au(surface)---P	Au(surface)---Br
Pd_2Au_{23}-TPP	2.682---2.786Å Avg. 2.730Å	2.808---2.878Å Avg. 2.844Å	2.793---2.998Å Avg. 2.880Å	2.281---2.290Å Avg. 2.280Å	2.497---2.670Å Avg. 2.607Å
Pd_2Au_{23}-TFPP	2.690---2.786Å Avg. 2.740Å	2.830---2.870Å Avg. 2.849Å	2.787---3.111Å Avg. 2.880Å	2.279---2.293Å Avg. 2.280Å	2.506---2.583Å Avg. 2.566Å
Diff.	-0.36%	-0.18%	0%	0%	1.60%

Table S2. Comparison of cell parameters between $Pd_2Au_{23}(TPP)_{10}Br_7$ and $Pd_2Au_{23}(TFPP)_{10}Br_7$. The corresponding cell units are highlights in Figure S3.

Cluster	Space group	Volume/Å^3	Unit cell dimensions		Z
$Pd_2Au_{23}(TPP)_{10}Br_7$	P 21/m	11590	a = 46.483 Å b = 77.477 Å c = 19.619 Å	α = 90° β = 102.95° γ = 90°	2
$Pd_2Au_{23}(TFPP)_{10}Br_7$	C 2/c	67904.4	a = 46.483 Å b = 77.477 Å c = 19.619 Å	α = 90° β = 106.04° γ = 90°	4

Table S3. Comparison of cell parameters between the singly-crystallized $Au_{11}(TFPP)_7Br_3$ and cocrystallized $Pd_1Au_9(TFPP)_6Br_3$@$Au_{11}(TFPP)_7Br_3$.

Cluster	Space group	Volume/Å^3	Unit cell dimensions		Z
$Au_{11}(TFPP)_7Br_3$	R 3	9775.7	a = 26.031 Å b = 26.031 Å c = 16.659 Å	α = 90° β = 90° γ = 120°	3
$Pd_1Au_9(TFPP)_6Br_3$@ $Au_{11}(TFPP)_7Br_3$	R 3	9623.9	a = 26.403 Å b = 26.403 Å c = 15.941 Å	α = 90° β = 90° γ = 120°	3

Table S4. Crystal data and structure refinement for the $Pd_2Au_{23}(TFPP)_{10}Br_7$.

Crystal system	monoclinic
Space group	C2/c
a/Å	46.48300
b/Å	77.47700
c/Å	19.61900
α/°	90
β/°	104.0600
γ/°	90
Volume/Å^3	67904
Z	4
Pcalc(g/cm^3)	2.482
μ/mm^{-1}	31.130
F(000)	45252.0
Radiation	CuKa (1.54186)
Index ranges	-55 <= h <= 55, -29 <= k <= 90, -22 <= l <= 23
Final R indexes [I>=2σ (I)]	R_1 = 0.0670 wR_2 = 0.1776
Final R indexes [all data]	R_1 = 0.0893 wR_2 = 0.1928

Table S5. Crystal data and structure refinement for the $Au_{11}(TFPP)_7Br_3$.

Crystal system	trigonal
Space group	R 3
a/Å	26.03100
b/Å	26.03100
c/Å	16.65900
α/°	90
β/°	90
γ/°	120
Volume/Å^3	9776
Z	3
Pcalc(g/cm^3)	2.354
μ/mm^{-1}	25.174
F(000)	6324.0
Radiation	CuKa (1.54186)
Index ranges	-28 <= h <= 31, -31 <= k <= 27, -10 <= l <= 20
Final R indexes [I>=2σ (I)]	R_1 = 0.0346 wR_2 = 0.0856
Final R indexes [all data]	R_1 = 0.0376 wR_2 = 0.0866

Table S6. Crystal data and structure refinement for the cocrystallized $Pd_1Au_9(TFPP)_6Br_3@Au_{11}(TFPP)_7Br_3$.

Crystal system	trigonal
Space group	R 3
a/Å	26.40300
b/Å	26.40300
c/Å	15.94100
α/°	90
β/°	90
γ/°	120
Volume/Å^3	9624
Z	3
Pcalc(g/cm^3)	2.063
μ/mm^{-1}	22.859
F(000)	2331.0
Radiation	CuKa (1.54186)
Index ranges	-23 <= h <= 30, -29 <= k <= 10, -18 <= l <= 17
Final R indexes [I>=2σ (I)]	R_1 = 0.1121 wR_2 = 0.2755
Final R indexes [all data]	R_1 = 0.1134 wR_2 = 0.2784