Supporting Information:

Understanding the Decomposition Process of $Pt_1Ag_{24}(SPhCl_2)_{18}$ Nanocluster at Atomic Level

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Notes: The authors declare no competing financial interest.

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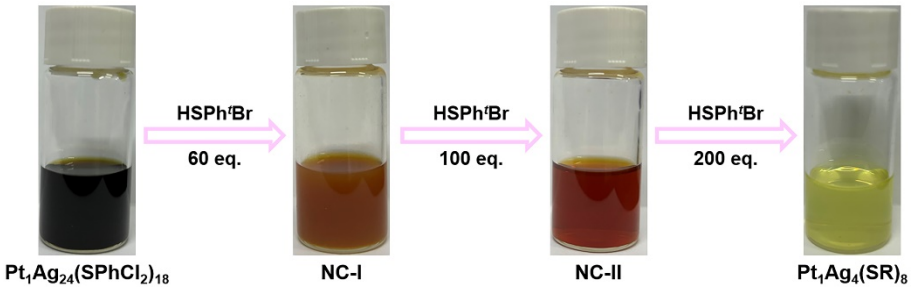

Fig. S1 The color change of the solution during the conversion from $\mathbf{Pt_1Ag_{24}(SPhCl_2)_{18}}$ to $\mathbf{Pt_1Ag_4(SR)_8}$.

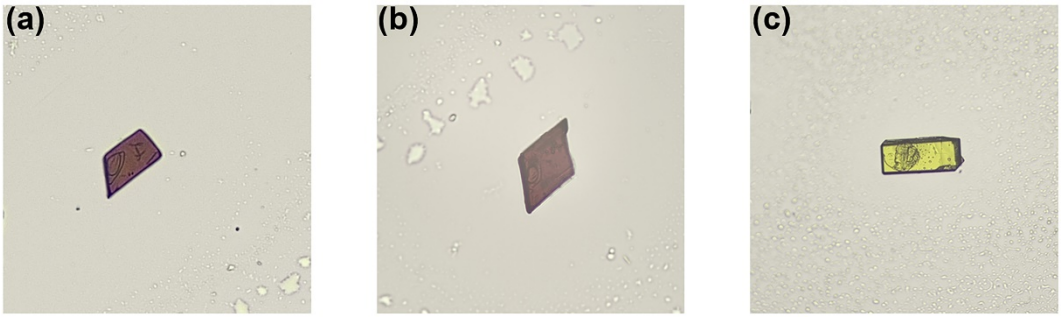

Fig. S2 The optical microscopic image of the single crystals of the **NC-I, NC-II and** $\mathbf{Pt_1Ag_4}$. (a) **NC-I**; (b) **NC-II**; (c) $\mathbf{Pt_1Ag_4}$.

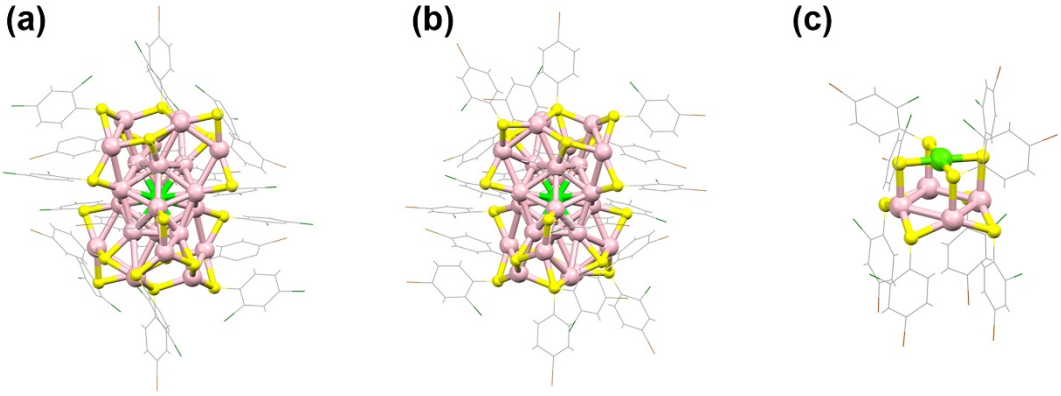

Fig. S3 The overall structure of the **NC-I**, **NC-II** nanoclusters and $\mathbf{Pt_1Ag_4}$ complex. (a) **NC-I**; (b) **NC-II**; (c) $\mathbf{Pt_1Ag_4}$. Color labels: bright green = Pt; pink = Ag; yellow = S; blue = Cl; brown = Br; grey = C; white = H.

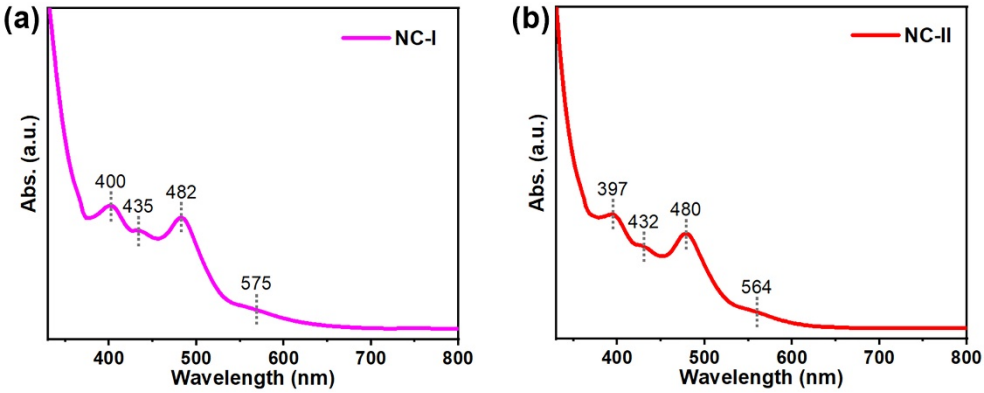

Fig. S4 The UV-vis absorption spectra of the **NC-I** and **NC-II** crystals in CH_2Cl_2. (a) **NC-I**; (b) **NC-II**.

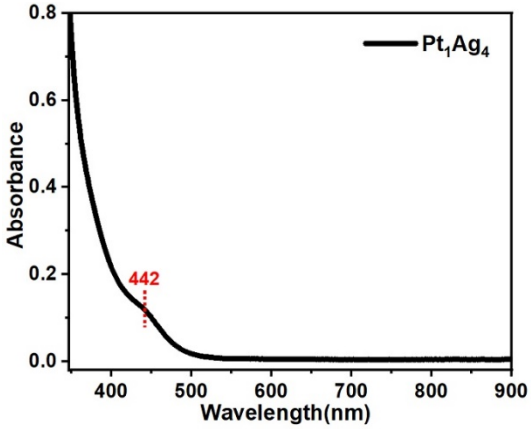

Fig. S5 The UV-vis absorption spectrum of the $\mathbf{Pt_1Ag_4}$ crystals in CH_2Cl_2.

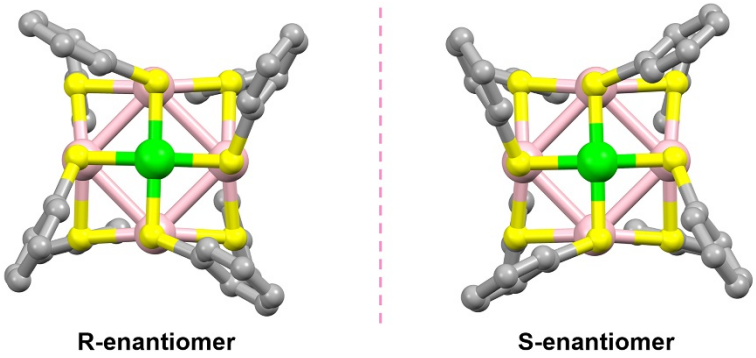

Fig. S6 X-ray structures of the two $\mathbf{Pt_1Ag_4}$ enantiomers viewed from the top. All H, C, Br and Cl atoms are omitted for clarity. Color labels: bright green = Pt; pink = Ag; yellow = S; grey = C.

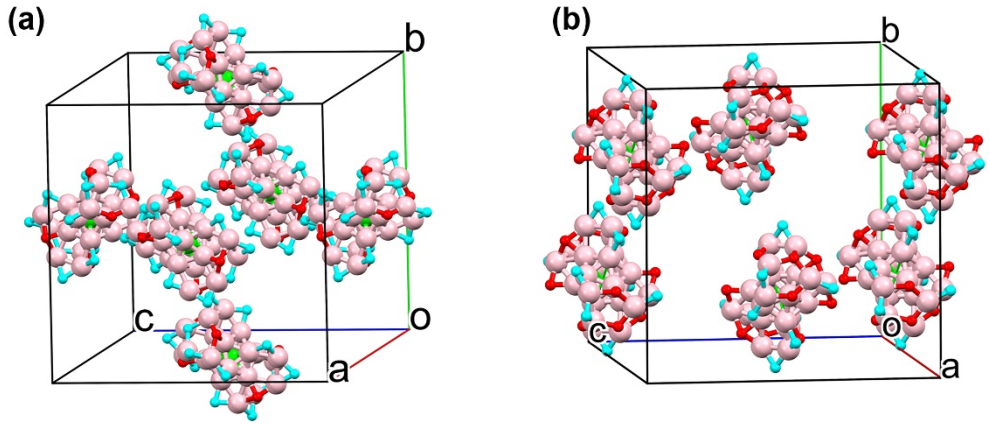

Fig. S7 A unit cell in the **NC-I** and **NC-II** single crystals. (a) **NC-I**; (b) **NC-II**. All H atoms, C atoms, Br atoms, Cl atoms and PPh_4^+ are omitted for clarity. Color labels: bright green = Pt; pink = Ag; red = 4-SPhBr; turquois = 2,4-$SPhCl_2$ and 4-SPhBr.

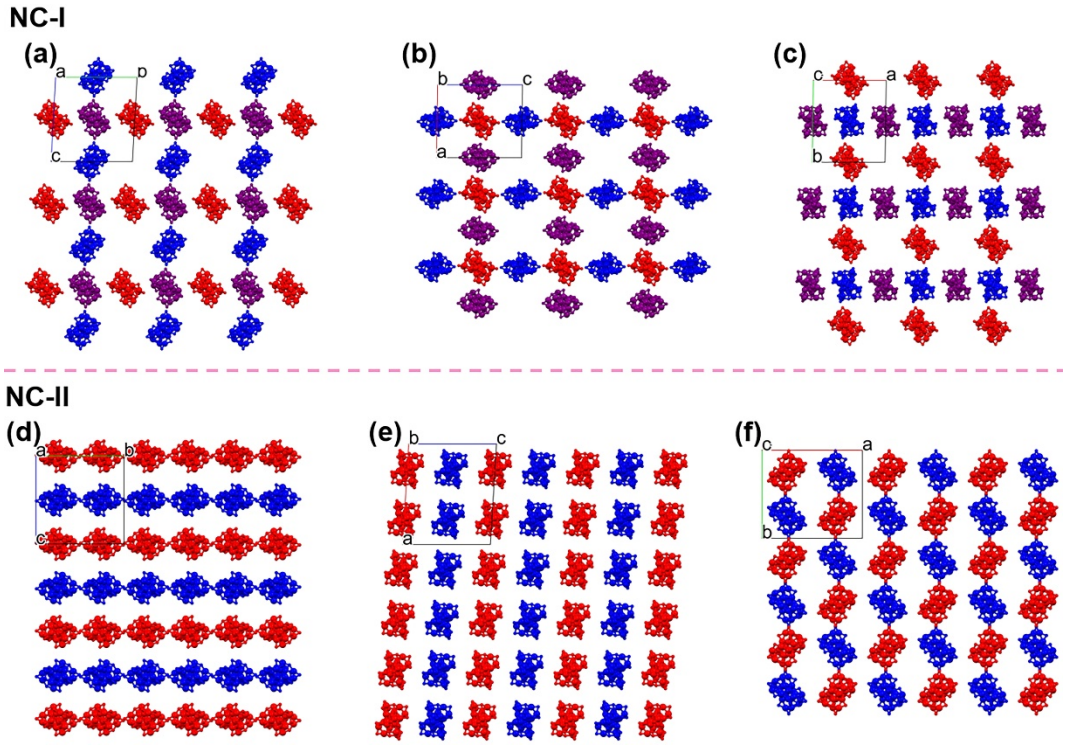

Fig. S8 Packing mode of **NC-I** and **NC-II** in the crystals shown. (a) and (d) along the a axis; (b) and (e) along the b axis; (c) and (f) along the c axis. All H atoms, C atoms and PPh_4^+ are omitted for clarity. The cluster molecules arranged in different directions show different colors.

Section 2. Supporting Tables

Table S1. The crystal structure parameters for **NC-I**.

Empirical formula	$C_{184}H_{120.67}Ag_{24}Br_{12.49}Cl_{15.03}P_{2.67}PtS_{20}$
Formula weight	7369.73
Temperature/K	120
Crystal system	triclinic
Space group	*P*-1
a/Å	26.638
b/Å	29.956
c/Å	31.053
α/°	90.09
β/°	90.67
γ/°	90.79
Volume/Å^3	24739.4
Z	3
ρ_{calc}g/cm^3	1.484
μ/mm^{-1}	16.342
F(000)	10449.0
Crystal size/mm^3	0.11 × 0.08 × 0.07
Radiation	Cu Kα (λ = 1.54186)
2Θ range for data collection/°	6.638 to 139.518
Index ranges	-32⩽h⩽29, -36⩽k⩽19, -33⩽l⩽37
Reflections collected	165059
Independent reflections	90081 [R_{int} = 0.0487, R_{sigma} = 0.0557]
Data/restraints/parameters	90081/3301/3334
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0607, wR_2 = 0.1650
Final R indexes [all data]	R_1 = 0.0909, wR_2 = 0.1850
Largest diff. peak/hole / e Å^{-3}	1.49/-2.32

Table S2. The crystal structure parameters for **NC-II**.

Empirical formula	$C_{216}H_{134}Ag_{24}Br_{17.72}Cl_{4.56}P_4PtS_{20}$
Formula weight	7855.93
Temperature/K	120.15
Crystal system	monoclinic
Space group	*C*2/*c*
a/Å	32.937
b/Å	28.819
c/Å	28.779
α/°	90
β/°	93.52
γ/°	90
Volume/Å^3	27265.8
Z	4
ρ_{calc}g/cm^3	1.914
μ/mm^{-1}	19.837
F(000)	14855.0
Crystal size/mm^3	0.1 × 0.08 × 0.06
Radiation	Cu Kα (λ = 1.54186)
2Θ range for data collection/°	8.604 to 139.508
Index ranges	-39≤h≤38, -31≤k≤35, -14≤l≤34
Reflections collected	91043
Independent reflections	25046 [R_{int} = 0.0827, R_{sigma} = 0.0770]
Data/restraints/parameters	25046/181/1342
Goodness-of-fit on F^2	0.946
Final R indexes [I>=2σ (I)]	R_1 = 0.0561, wR_2 = 0.1403
Final R indexes [all data]	R_1 = 0.0851, wR_2 = 0.1526
Largest diff. peak/hole / e Å^{-3}	1.85/-1.82

Table S3. The crystal structure parameters for **Pt_1Ag_4**.

Empirical formula	$C_{96}H_{64}Ag_4Br_{3.69}Cl_{8.62}P_2PtS_8$
Formula weight	2762.91
Temperature/K	170
Crystal system	triclinic
Space group	*P*-1
a/Å	17.7833(12)
b/Å	17.8696(12)
c/Å	18.2588(12)
α/°	110.766(2)
β/°	112.206(2)
γ/°	90.922(2)
Volume/Å^3	4946.9(6)
Z	2
ρ_{calc}g/cm^3	1.855
μ/mm^{-1}	4.156
F(000)	2679.0
Crystal size/mm^3	0.12 × 0.11 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.82 to 49.998
Index ranges	-21≤h≤19, -21≤k≤19, 0≤l≤21
Reflections collected	17189
Independent reflections	17189 [R_{sigma} = 0.0547]
Data/restraints/parameters	17189/1658/952
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0994, wR_2 = 0.2393
Final R indexes [all data]	R_1 = 0.1436, wR_2 = 0.2635
Largest diff. peak/hole / e Å^{-3}	4.86/-1.72

Table S4. The occupancy ratio of 2,4-$SPhCl_2$ and 4-SPhBr units in **NC-I**, **NC-II** and **Pt_1Ag_4**. (Notably, the occupancy ratios of **NC-I** are the average occupancy ratios among the three cluster molecules in the single crystal).

Nanoclusters	**Sites**	**2,4-$SPhCl_2$ (occupancy ratio)**	**4-SPhBr (occupancy ratio)**
NC-I	ligand-1	50%	50%
NC-II	ligand-1	14%	86%
NC-I	ligand-2	42%	58%
NC-II	ligand-2	24%	76%
NC-I	ligand-3	79%	21%
NC-II	ligand-3	25%	75%
NC-I	ligand-4	71.6%	28.4%
NC-II	ligand-4	0%	100%
NC-I	ligand-5	60.7%	39.3%
NC-II	ligand-5	22%	78%
NC-I	ligand-6	62.3%	37.7%
NC-II	ligand-6	29%	71%
NC-I	ligand-7	0%	100%
NC-II	ligand-7	0%	100%
NC-I	ligand-8	0%	100%
NC-II	ligand-8	0%	100%
NC-I	ligand-9	0%	100%
NC-II	ligand-9	0%	100%
NC-I	ligand-10	10%	90%
NC-II	ligand-10	0%	100%
Pt_1Ag_4		46%	54%
		47%	53%
		67%	33%
		45%	55%
		55%	45%
		59%	41%
		53%	47%
		59%	41%

Table S5. S-Ag bond lengths associated with the ligand in **NC-I** and **NC-II**. (Notably, the bond lengths of **NC-I** are the average bond lengths among the three cluster molecules in the single crystal).

S-Ag Bonds in NC-I	Average bond lengths (Å) in NC-I	S-Ag Bonds in NC-II	bond lengths (Å) in NC-II
$S_{ligand-1}$-Ag	2.433	$S_{ligand-1}$-Ag	2.486
$S_{ligand-1}$-Ag	2.516	$S_{ligand-1}$-Ag	2.411
$S_{ligand-2}$-Ag	2.434	$S_{ligand-2}$-Ag	2.445
$S_{ligand-2}$-Ag	2.499	$S_{ligand-2}$-Ag	2.488
$S_{ligand-3}$-Ag	2.436	$S_{ligand-3}$-Ag	2.438
$S_{ligand-3}$-Ag	2.491	$S_{ligand-3}$-Ag	2.489
$S_{ligand-4}$-Ag	2.481	$S_{ligand-4}$-Ag	2.482
$S_{ligand-4}$-Ag	2.45	$S_{ligand-4}$-Ag	2.444
$S_{ligand-5}$-Ag	2.458	$S_{ligand-5}$-Ag	2.459
$S_{ligand-5}$-Ag	2.454	$S_{ligand-5}$-Ag	2.468
$S_{ligand-6}$-Ag	2.448	$S_{ligand-6}$-Ag	2.465
$S_{ligand-6}$-Ag	2.446	$S_{ligand-6}$-Ag	2.459
$S_{ligand-7}$-Ag	2.489	$S_{ligand-7}$-Ag	2.488
$S_{ligand-7}$-Ag	2.494	$S_{ligand-7}$-Ag	2.490
$S_{ligand-7}$-Ag	2.567	$S_{ligand-7}$-Ag	2.579
$S_{ligand-8}$-Ag	2.477	$S_{ligand-8}$-Ag	2.499
$S_{ligand-8}$-Ag	2.470	$S_{ligand-8}$-Ag	2.469
$S_{ligand-8}$-Ag	2.629	$S_{ligand-8}$-Ag	2.604
$S_{ligand-9}$-Ag	2.515	$S_{ligand-9}$-Ag	2.539
$S_{ligand-9}$-Ag	2.483	$S_{ligand-9}$-Ag	2.467
$S_{ligand-9}$-Ag	2.596	$S_{ligand-9}$-Ag	2.612
$S_{ligand-10}$-Ag	2.552	$S_{ligand-10}$-Ag	2.542
$S_{ligand-10}$-Ag	2.552	$S_{ligand-10}$-Ag	2.557
$S_{ligand-10}$-Ag	2.505	$S_{ligand-10}$-Ag	2.543