

Supporting information for

**Understanding the Ligand's Effects on Intra-cluster and Inter-cluster
Assembly**

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Notes: The authors declare no competing financial interest.

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Figures S1-S11

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Figure S1. An optical microscopic image of the single crystals of **Cd₁₂Ag₃₂-2**.



Figure S2. An optical microscopic image of the single crystals of **Cd₁₂Ag₃₂-1**.

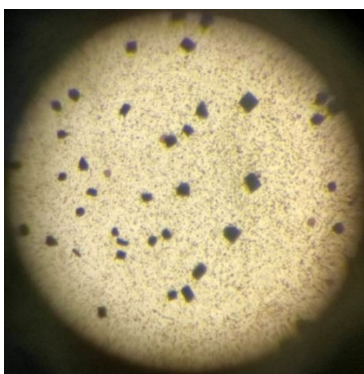


Figure S3. An optical microscopic image of the single crystals of **Cd₁₂Ag₃₂-3**.

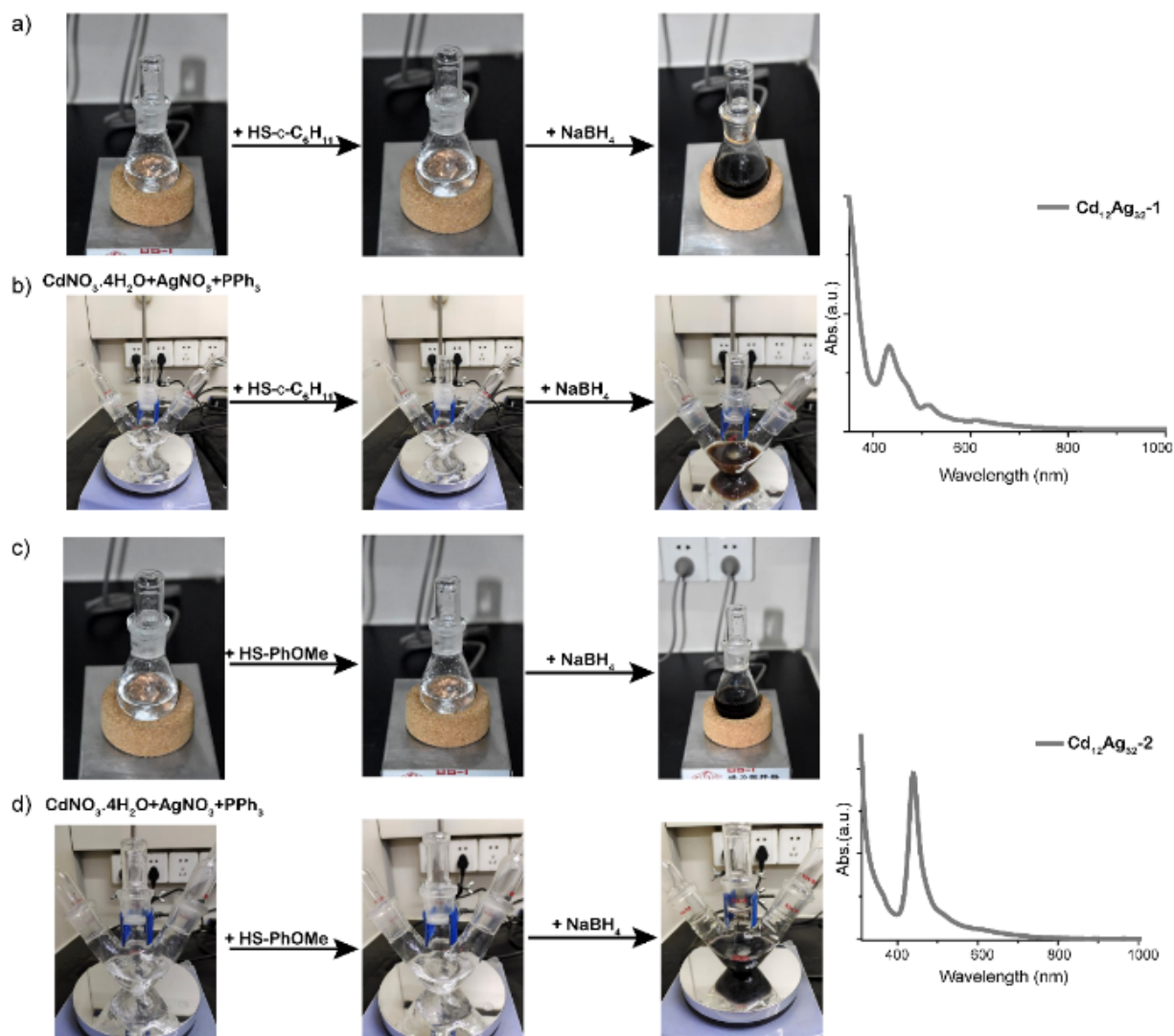


Figure S4. The digital photographs describing the synthesis of Cd₁₂Ag₃₂-1 and Cd₁₂Ag₃₂-2, respectively. a), c) under Ar₂ atmosphere; b), d) in air atmosphere.

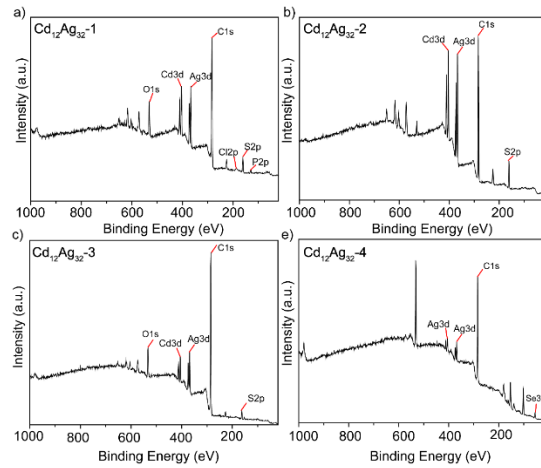


Figure S5. X-ray photoelectron spectrum (XPS) of the nanocluster. a), $\text{Cd}_{12}\text{Ag}_{32}$ -1, b), $\text{Cd}_{12}\text{Ag}_{32}$ -2, c), $\text{Cd}_{12}\text{Ag}_{32}$ -3, d), $\text{Cd}_{12}\text{Ag}_{32}$ -4.

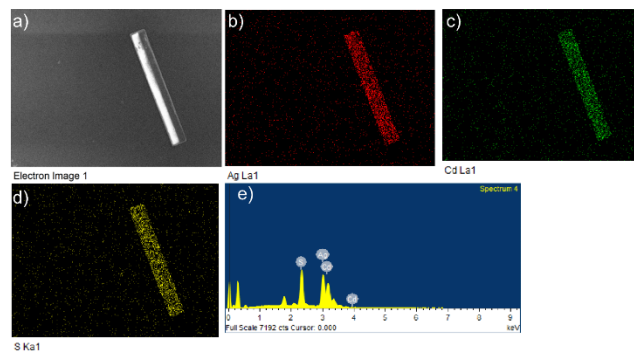


Figure S6. (a) SEM image of a small deformed single crystal of $\text{Cd}_{12}\text{Ag}_{32}$ -1. (b-d) are the elemental maps of Ag, Cd and S, respectively. (e) EDS spectrum, confirming the presence of above elements in the cluster, which is consistent with the cluster composition obtained by SCXRD data.

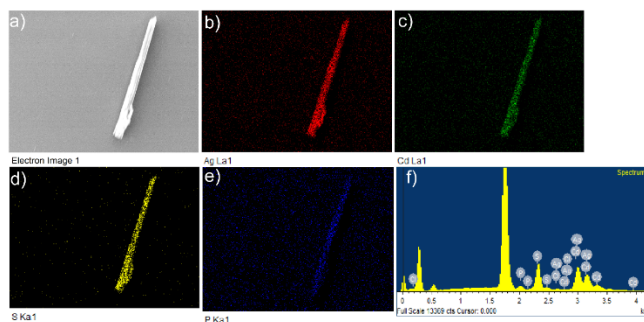


Figure S7. (a) SEM image of a small deformed single crystal of $\text{Cd}_{12}\text{Ag}_{32}$ -2. (b-d) are the elemental maps of Ag, Cd and S, respectively. (e) EDS spectrum, confirming the presence of above elements in the cluster, which is consistent with the cluster composition obtained by SCXRD data.

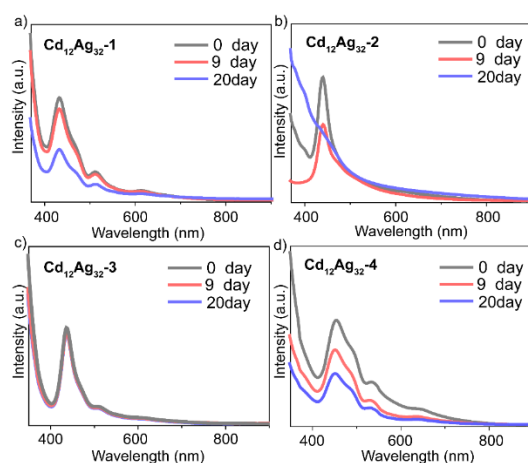


Figure S8. Monitoring the ambient stability of **Cd₁₂Ag₃₂-1**, **Cd₁₂Ag₃₂-2**, **Cd₁₂Ag₃₂-3** and **Cd₁₂Ag₃₂-4** in solution, respectively, using UV-vis spectroscopy.

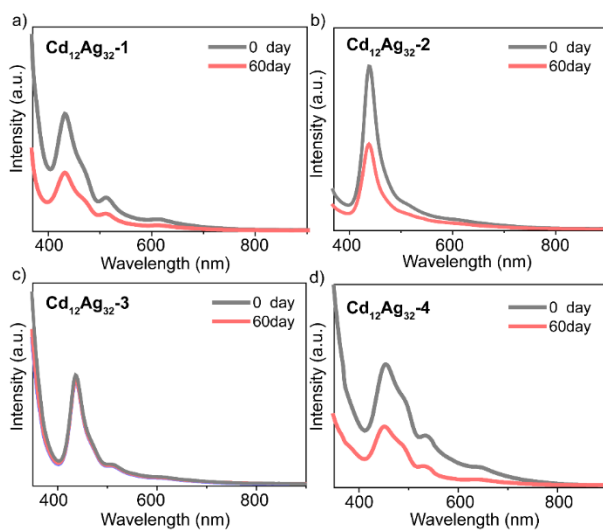


Figure S9. Monitoring the ambient stability of **Cd₁₂Ag₃₂-1**, **Cd₁₂Ag₃₂-2**, **Cd₁₂Ag₃₂-3** and **Cd₁₂Ag₃₂-4** in solid state, respectively, using UV-vis spectroscopy.

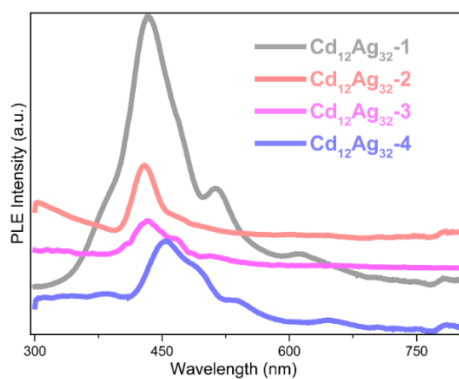


Figure S10. PL excitation (PLE) spectra of **Cd₁₂Ag₃₂-1**, **Cd₁₂Ag₃₂-2** and **Cd₁₂Ag₃₂-3**.

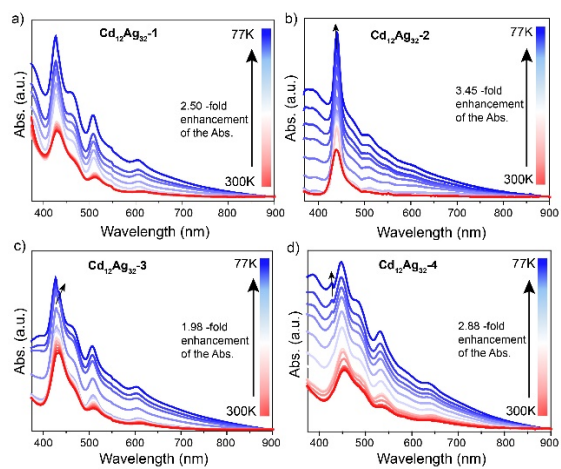


Figure S11. Temperature-dependent UV-vis spectra of Cd₁₂Ag₃₂-1, Cd₁₂Ag₃₂-2, Cd₁₂Ag₃₂-3 and Cd₁₂Ag₃₂-4.

Table S1. The atomic ratio of Ag and Cd in **Cd₁₂Ag₃₂-1** and **Cd₁₂Ag₃₂-2** was calculated from X-ray photoelectric spectroscopy (XPS) and ICP measurements.

Cd₁₂Ag₃₂-1	Cd (%)	Ag (%)
XPS results	31.52	68.48
ICP results	31.39	68.61
Cd₁₂Ag₃₂-1 theoretical results	18/58 (31.03)	40/58 (68.97)
Cd₁₂Ag₃₂-2	Cd (%)	Ag (%)
XPS results	27.6	72.4
ICP results	27.55	72.45
Cd₁₂Ag₃₂-2 theoretical results	12/44 (27.27)	32/44(72.73)
Cd₁₂Ag₃₂-3	Cd (%)	Ag (%)
XPS results	27.01	72.99
ICP results	27.70	72.30
Cd₁₂Ag₃₂-3 theoretical results	12/44 (27.27)	32/44(72.73)

Table S2. List of bond lengths in **Cd₁₂Ag₃₂**, **Cd₁₂Ag₃₂-2** and **Cd₁₂Ag₃₂-3**.

Bond type/Location	Cd₁₂Ag₃₂-1		Cd₁₂Ag₃₂-2		Cd₁₂Ag₃₂-3		Cd₁₂Ag₃₂-4	
	range (Å)	average (Å)	range (Å)	average (Å)	range (Å)	average (Å)	range (Å)	average (Å)
Ag-Ag/(within Ag ₄ inner core)	2.845-2.857	2.851	2.853-2.909	2.876	2.811-2.811	2.811	2.834-2.863	2.847
Ag-Ag/(Ag ₄ -Ag ₂₄ layer)	2.675-3.071	2.831	2.668-3.172	2.841	2.772-3.031	2.828	2.673-3.156	2.838
Ag-Ag/(within the Ag ₂₄ layer)	2.813-3.173	2.949	2.791-3.16	2.956	2.772-3.061	2.913	2.805-3.160	2.956
Ag-S/Se/(Ag ₂₄ layer-S/Se)	2.492-2.525	2.506	2.403-2.572	2.502	2.497-2.518	2.507	2.575-2.640	2.604
Ag-S/Se/(within the ligand motif)	2.618-2.624	2.611	2.418-2.562	2.495	2.721-2.721	2.721	2.571-2.638	2.600
Ag-Cd/(within the ligand motif)	4.10-4.24	4.18	3.334-3.633	3.51	3.571-3.571	3.571	3.520-3.701	3.63
Cd-S/Se/(within the ligand motif)	2.451-2.504	2.535	2.408-2.669	2.492	2.547-2.646	2.583	2.565-2.734	2.643
Ag-P/(within the ligand motif)	2.503-2.516	2.506	-	-	-	-	-	-

Table S3. Crystal data and structure refinement of **Cd₁₂Ag₃₂-1**.

Empirical formula	Cd ₁₈ Ag ₄₀ Cl ₈ P ₁₂ S ₄₈ C ₅₅₂ H ₄₆₈ O ₄₈
Formula weight	16401.97
Temperature/K	170 K
Crystal system	trigonal
Space group	P-3
a/Å	33.2637(4)
b/Å	33.2637(4)
c/Å	28.1094(3)
α /°	90
β /°	90
γ /°	120
Volume/Å ³	26935.4(7)
Z	1
ρ _{calc} g/cm ³	1.510
μ/mm	15.853
F(000)	11892
Crystal size/mm ³	0.15 x 0.1 x 0.08
Radiation	CuKα (1.54186 Å)
2θ range for data collection/°	4.060 to 64.992
Index ranges	-38 ≤ h ≤ 38, -30 ≤ k ≤ 39, -33 ≤ l ≤ 14
Reflections collected	83427
Independent reflections	30227[R _{int} = 0.0373, R _{sigma} = 0.0541]
Data/restraints/parameters	30227/3810/1367
Goodness-of-fit on F ²	1.154
Final R indexes [I ≥ 2σ(I)]	R1 = 0.0855, wR2 = 0.2681
Final R indexes [all data]	R1 = 0.1151, wR2 = 0.2894
Largest diff. peak/hole/eÅ ⁻³	21.837/-2.094

Table S4. Crystal data and structure refinement of **Cd₁₂Ag₃₂-2**.

Empirical formula	C ₂₁₆ H ₃₉₀ Ag ₃₂ Cd ₁₂ S ₃₆
Formula weight	9842.06
Temperature/K	170K
Crystal system	orthorhombic
Space group	Pca21
a/Å	30.8174(5)
b/Å	28.5803(9)
c/Å	39.1573(7)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	34488.6(14)
Z	4
ρ_{calc} g/cm ³	1.722
μ /mm	22.257
F(000)	17368
Crystal size/mm ³	0.12 x 0.1 x 0.08
Radiation	CuK α (1.54184 Å)
2 θ range for data collection/°	2.868 to 64.997
Index ranges	-35 \leq h \leq 36, -32 \leq k \leq 33, -30 \leq l \leq 40
Reflections collected	109831
Independent reflections	44911[R _{int} = 0.1318, R _{sigma} = 0.1380]
Data/restraints/parameters	44911/3951/2666
Goodness-of-fit on F ²	0.970
Final R indexes [I \geq 2 σ (I)]	R1 = 0.0923, wR2 = 0.2333
Final R indexes [all data]	R1 = 0.1419, wR2 = 0.2655
Largest diff. peak/hole/eÅ ⁻³	1.957/-1.234

Table S5. Crystal data and structure refinement of **Cd₁₂Ag₃₂S₃₆**.

Empirical formula	Ag ₃₂ Cd ₁₂ S ₃₆
Formula weight	5954.80
Temperature/K	120K
Crystal system	cubic
Space group	Fm-3
a/Å	32.067(8)
b/Å	32.067(8)
c/Å	32.067(8)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	32975(25)
Z	4
ρ_{calc} g/cm ³	1.199
μ /mm	23.040
F(000)	10624
Crystal size/mm ³	0.1 x 0.1 x 0.1
Radiation	CuK α (1.54186 Å)
2 θ range for data collection/°	4.573 to 56.784
Index ranges	-28 \leq h \leq 24, -33 \leq k \leq 19, -34 \leq l \leq 9
Reflections collected	5301
Independent reflections	1857[R _{int} = 0.0713, R _{sigma} = 0.0846]
Data/restraints/parameters	1857/0/61
Goodness-of-fit on F ²	0.920
Final R indexes [I \geq 2 σ (I)]	R1 = 0.0930, wR2 = 0.2571
Final R indexes [all data]	R1 = 0.1563, wR2 = 0.3163
Largest diff. peak/hole/eÅ ⁻³	0.733/-1.235