Electronic Supplementary Material (ESI) for Nanoscale Advances.

The definition of coordination number (CN)

The coordination number (CN) of Au-Au bonds was calculated according to the definition of connectivity proposed by Pei and Ma.[1] In detail, for each Au-Au bond, CN is 1, 0.75, 0.5, 0.25 and 0 when R_{Au-Au} (i.e. Au-Au distance) ranges from ≤3.1, (3.1, 3.2], (3.2,3.3], (3.3,3.4], and >3.4 Å. Due to the similar atomic radii of Au and Ag atoms, CN of Au-Ag bond is defined as the same as Au-Au bonds. Meanwhile, the connectivity of Au-P bond is 1, 0.75, 0.5, 0.25 and 0 when R_{Au-P} ranges from ≤2.4 , (2.4, 2.45], (2.45, 2.5], (2.5, 2.55], and >2.55 Å.

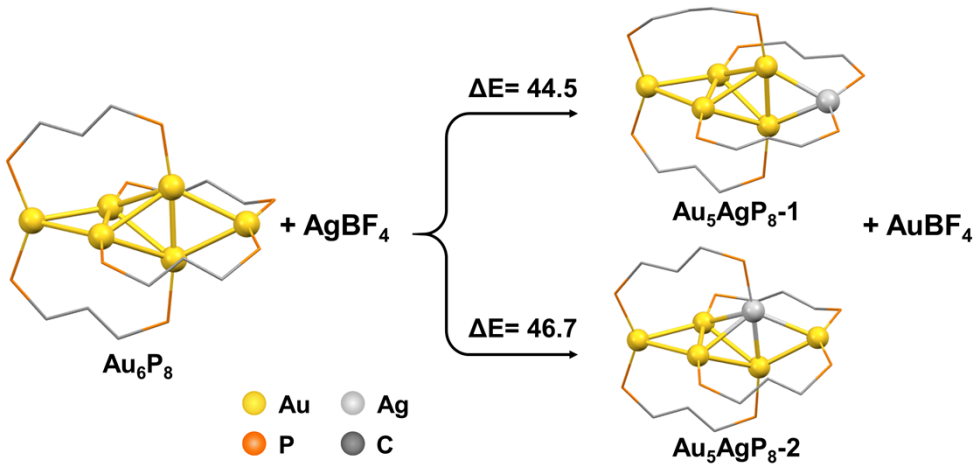
References

1. C. Liu, Y. Pei, H. Sun, *et al.,* The Nucleation and Growth Mechanism of Thiolate-Protected Au Nanoclusters. *J. Am. Chem. Soc.* 2015, **137**, 15809-15816.

Table S1. The Hirshfeld charge of metal atoms in **Au_6P_8**, **Au_6AgP_8-2**, **$Au_6Ag_2P_8$-4, $Au_6Ag_3P_8$-2,** and **$Au_6Ag_4P_8$-1** structures, the charge of Au^5 and Au^6 was highlighted in blue.

	Au_6P_8	**Au_6AgP_8-2**	**$Au_6Ag_2P_8$-4**	**$Au_6Ag_3P_8$-2**	**$Au_6Ag_4P_8$-1**
Au^1	-0.023	-0.018	-0.003	0.034	0.052
Au^2	-0.023	-0.008	0.009	0.026	0.037
Au^3	-0.031	0.032	-0.008	0.033	0.037
Au^4	-0.044	-0.021	-0.003	0.024	0.057
Au^5	0.002	0.057	0.086	0.114	0.143
Au^6	-0.009	0.035	0.083	0.109	0.116
Ag^1	-	0.077	0.057	0.123	0.179
Ag^2	-	-	0.062	0.107	0.137
Ag^3	-	-	-	0.144	0.076
Ag^4	-	-	-	-	0.324
[a]Avg. of M_n	-0.021	0.022	0.035	0.079	0.116
[b]Avg. of Au_4Ag_n	-0.030	-0.012	0.019	0.070	0.112

Note: [a]Avg. of M_n designates the average Hirshfeld charge of all metal atoms, while [b]Avg. of Au_4Ag_n denotes the average Hirshfeld charge of a core structure comprising Au^{1-4} and all Ag atoms (Au^5 and Au^6 are excluded for their low coordination number with the other metal atoms).



Scheme S1. The metal exchange of Ag^{+} with Au^{+} in **Au_6P_8**

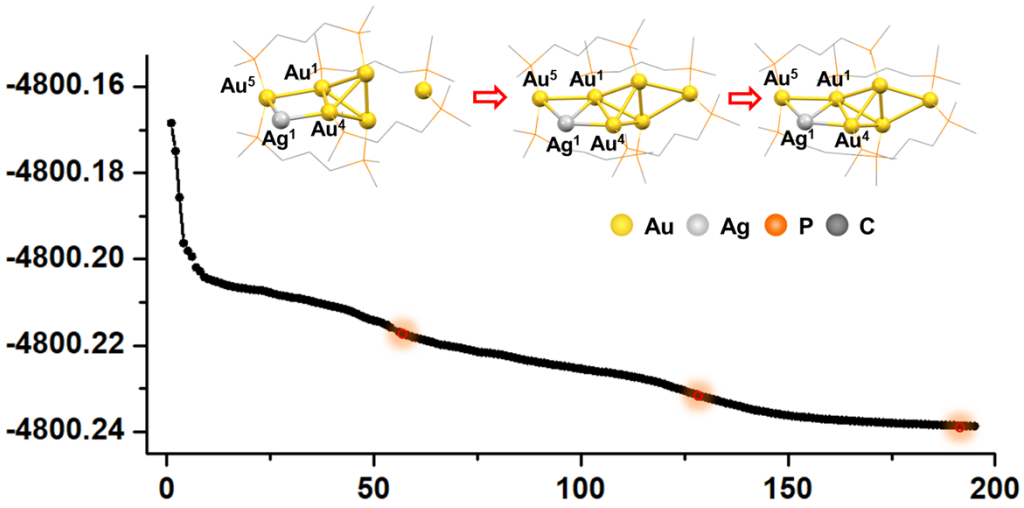


Figure S1. Geometry optimization energy profile of **Au_6AgP_8-2** and the selected intermediate structures.

.

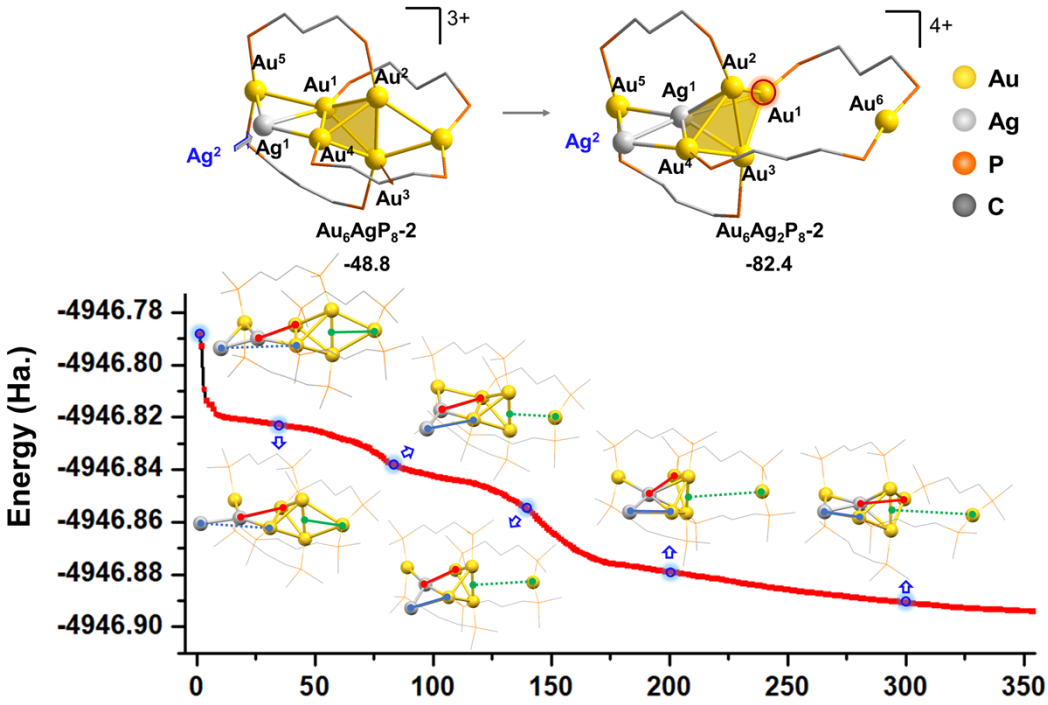


Figure S2. Geometry optimization energy profile of **$Au_6Ag_2P_8$-2** and the selected intermediate structures.

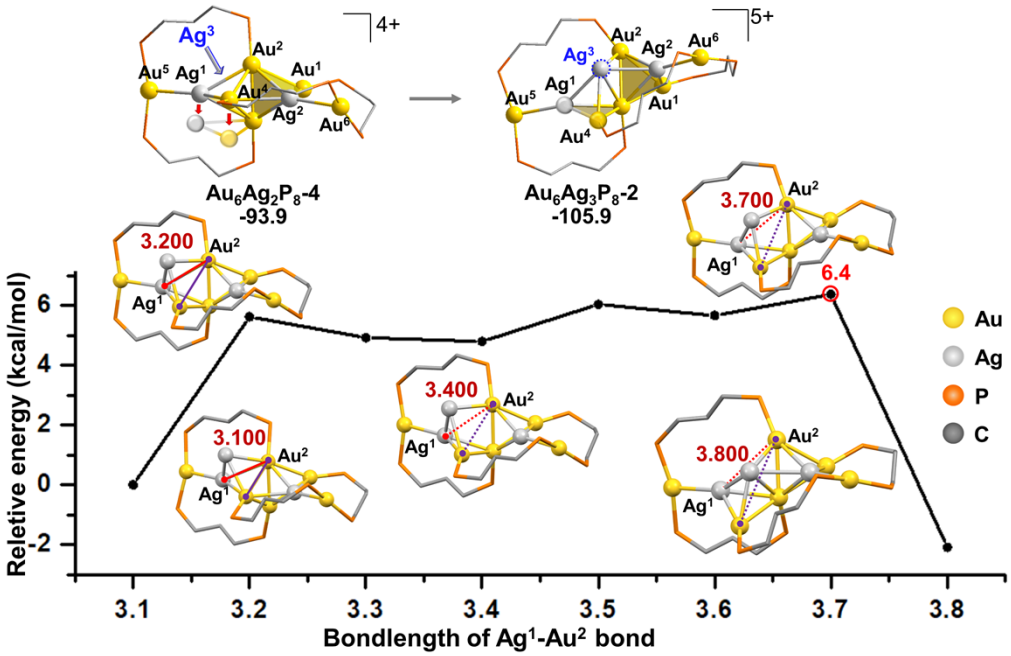
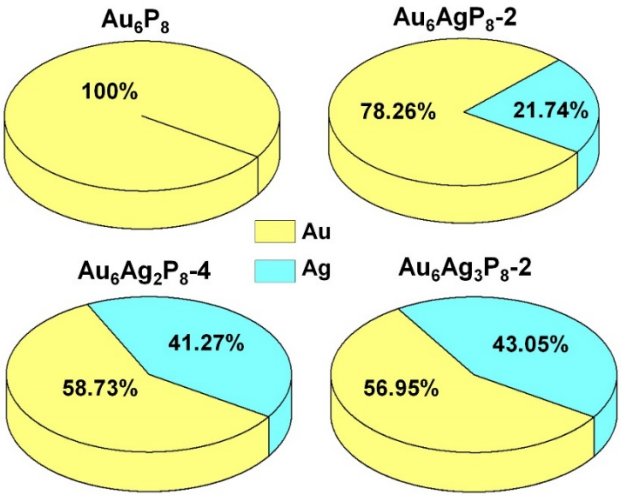


Figure S3. Constrained optimization profile by fixing Ag^1-Au^2 bond at different distances, and inset: illustrative diagram for the structural changes via inserting Ag^3 into the Au^2-Ag^1 bond.

Table S2. The CN of metal atoms in **Au_6P_8**, **Au_6AgP_8-2**, **$Au_6Ag_2P_8$-4, $Au_6Ag_3P_8$-1/2/3/4,** and **$Au_6Ag_4P_8$-1** structures, the charge of Au^5 and Au^6 was highlighted in blue.

	Au_6P_8	**Au_6AgP_8-2**	**$Au_6Ag_2P_8$-4**	**$Au_6Ag_3P_8$-1**	**$Au_6Ag_3P_8$-2**	**$Au_6Ag_3P_8$-3**	**$Au_6Ag_3P_8$-4**	**$Au_6Ag_4P_8$-1**
Au^1	4 (5)	5 (6)	4 (5)	3 (4)	3 (4)	2 (3)	3 (4)	3 (4)
Au^2	4 (5)	4 (5)	5 (6)	6 (7)	4 (5)	4 (5)	5.75 (6.75)	5 (6)
Au^3	4 (5)	5 (6)	5 (6)	4 (5)	6 (7)	4 (5)	4 (5)	5 (6)
Au^4	4 (5)	4 (5)	4 (5)	4 (5)	3 (4)	4 (5)	3.25 (4.25)	3 (4)
Au^5	2 (4)	2 (4)	1 (3)	1 (3)	1 (3)	1 (3)	1 (3)	1 (3)
Au^6	2 (4)	2 (4)	1 (3)	1 (3)	1 (3)	1 (3)	1 (3)	1 (3)
Ag^1	-	3 (3)	4 (4)	4 (4)	4 (4)	4 (4)	4 (4)	5 (5)
Ag^2	-	-	5 (5)	5 (5)	4 (4)	3 (3)	4 (4)	5 (5)
Ag^3	-	-	-	3 (3)	5 (5)	5 (5)	4 (4)	5 (5)
Ag^4	-	-	-	-	-	-	-	3 (3)
[a]Avg. of M_n	3.3 (4.7)	3.6 (4.7)	3.6 (4.6)	3.4 (4.3)	3.4 (4.3)	3.1 (4.0)	3.3 (4.2)	3.6 (4.4)
[b]Avg. of Au_4Ag_n	4.0 (5.0)	4.2 (5.0)	4.5 (5.2)	4.1 (4.7)	4.1 (4.7)	3.7 (4.3)	4.0 (4.6)	4.3 (4.8)

Note: [a]Avg. of M_n designates the average coordination number of all-metal atoms without the coordination of P, while [b]Avg. of Au_4Ag_n denotes the average coordination number of a core structure comprising Au^{1-4} and all Ag atoms (Au^5 and Au^6 are excluded for their low coordination number with the other metal atoms). The values in brackets refer to the case where P coordination is considered.



Scheme S2. The contribution of Au and Ag components in HOMO of Au_6Ag_n (n=0, 1, 2 and 3) cores in different clusters.

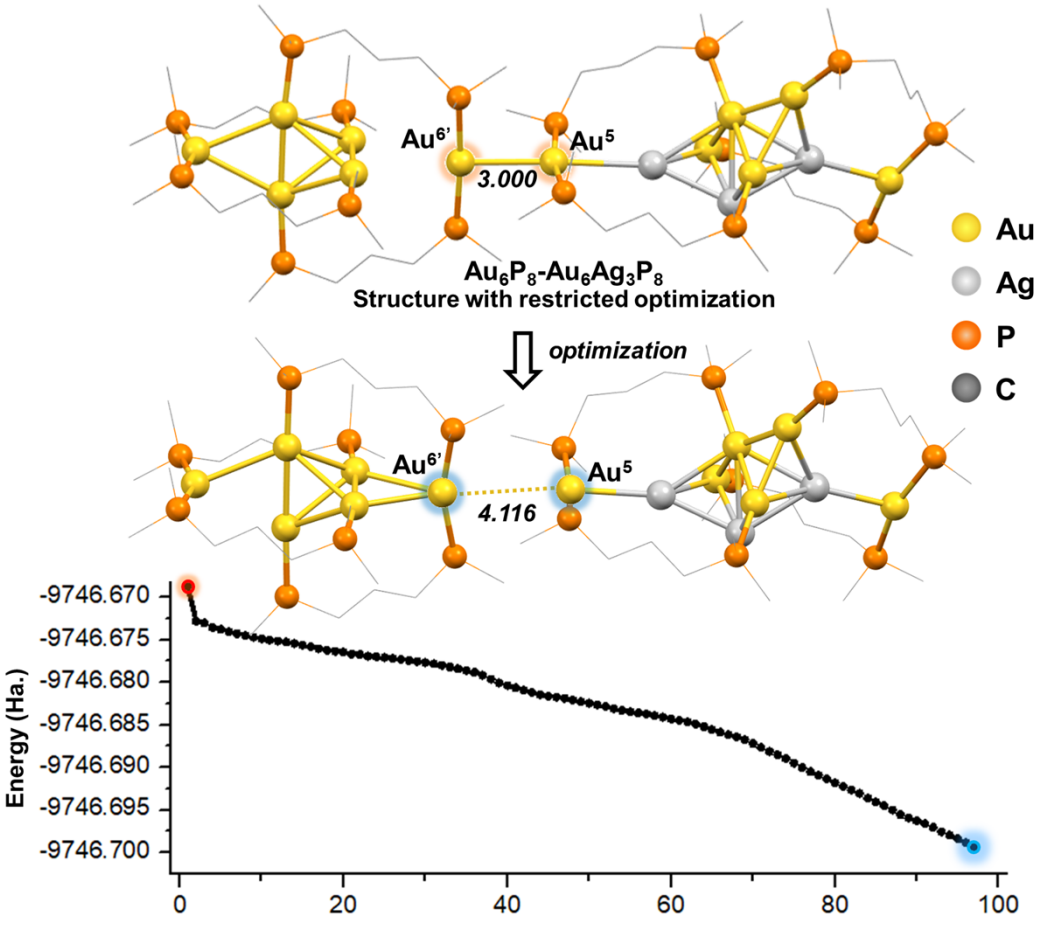


Figure S4. The energy curve for geometry optimization starting from constrained structure of **Au_6P_8-$Au_6Ag_3P_8$** (obtained via partial optimization by setting $Au^{6'}$-Au^5 at 3.0 Å). From the energy curve, it can be seen that the two cluster blocks gradually moves away during the geometry optimization, and collapse to a discrete state in a barrierless way.

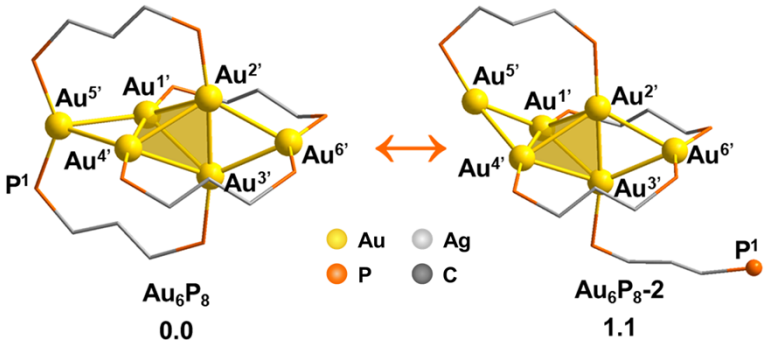
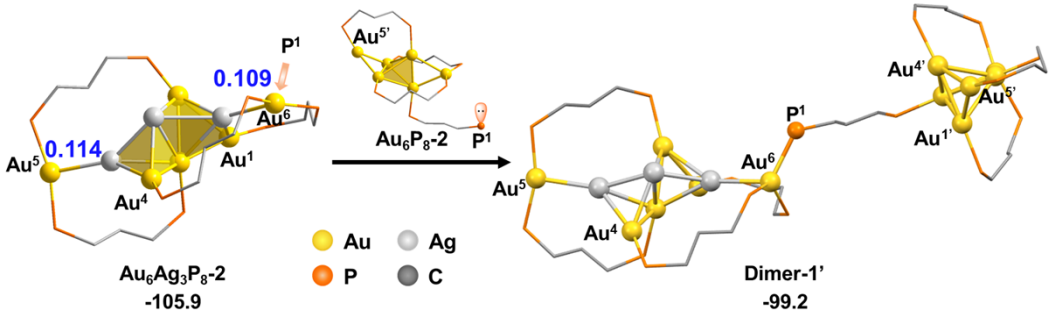


Figure S5. The process of Au_6P_8 to Au_6P_8-2. The terminal $Au^{5'}$ and P^1 atoms were both active for the subsequent size-growth process.



Scheme S3. The energy and structure change after the reaction of Au_6P_8-2 with $Au_6Ag_3P_8$-2 by coordination of P^1 to Au^6 atom.

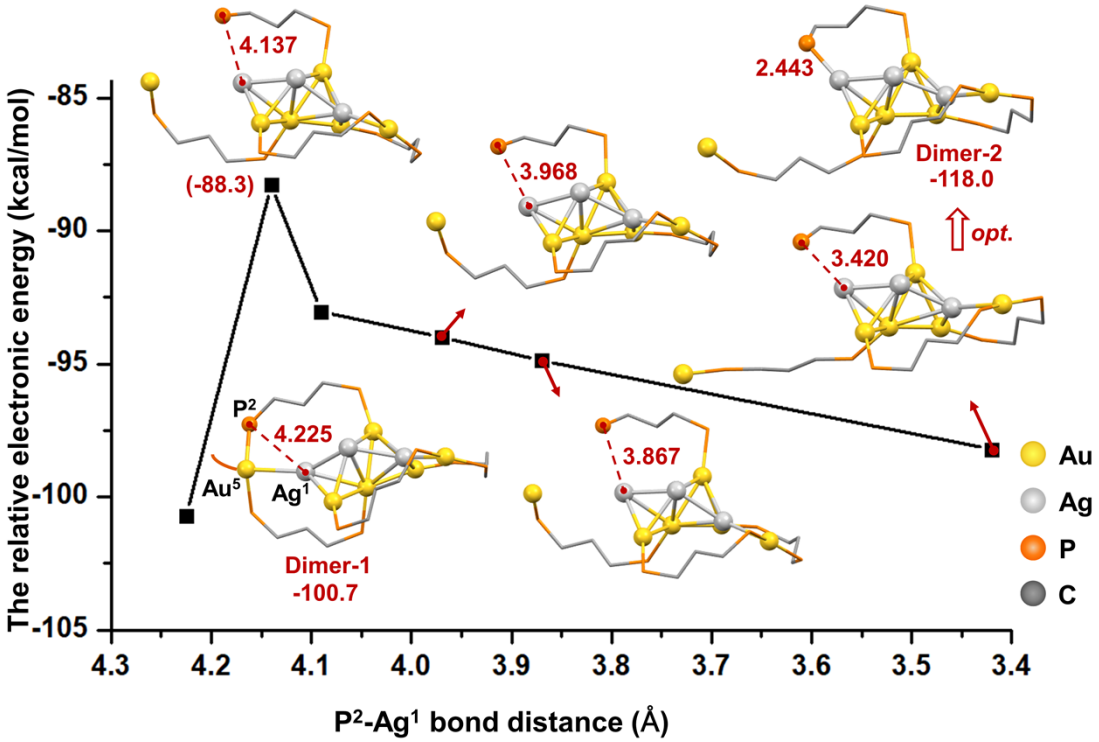


Figure S6. The energy profile for the 1,2-P^2 migration during the transformation from **Dimer-1** to **Dimer-2**. Each structure is partially optimized at a given P^2-Ag^1 bond length. For clarity, only the alloy cluster block has been shown.

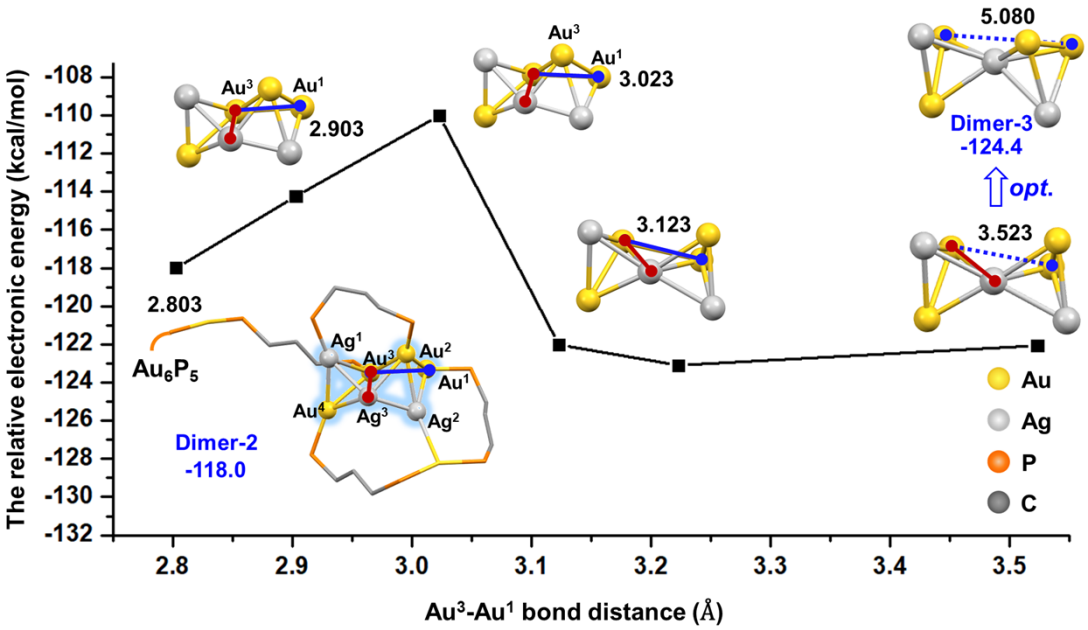


Figure S7. The partial optimization energy profile from **Dimer-2** to **Dimer-3** via fixing the Au^3-Au^1 bond at different distances. Except for the changing Ag_4Ag_3 blocks, all other structures were omitted.

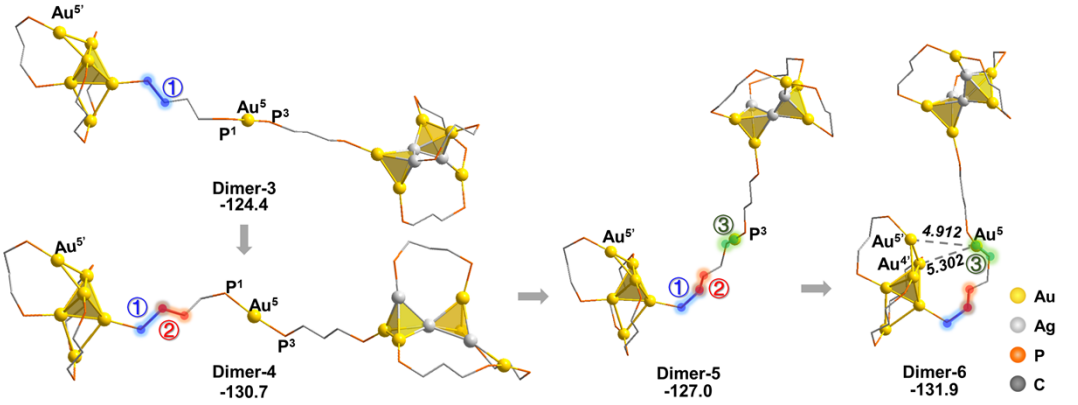


Figure S8. The process of **Dimer-3** to **Dimer-6**. The arms of the dangling P~P were highlighted in different colors and labeled with numbers.

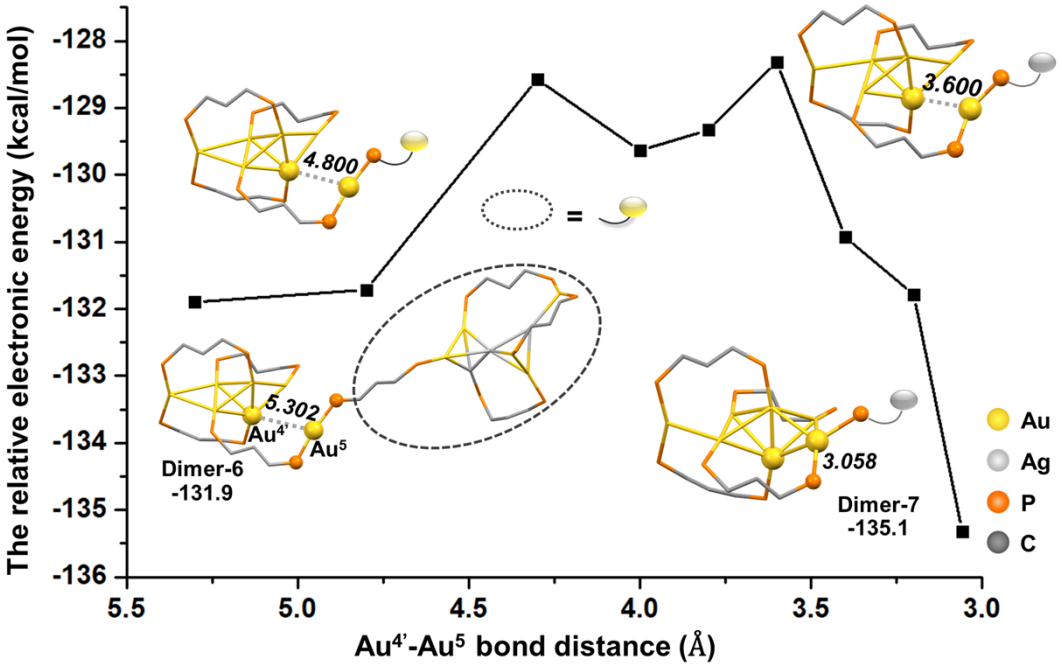
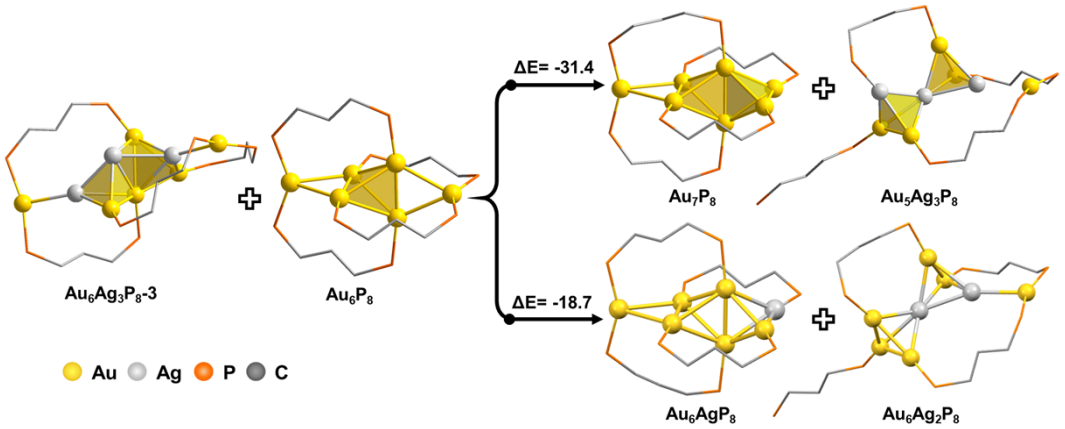
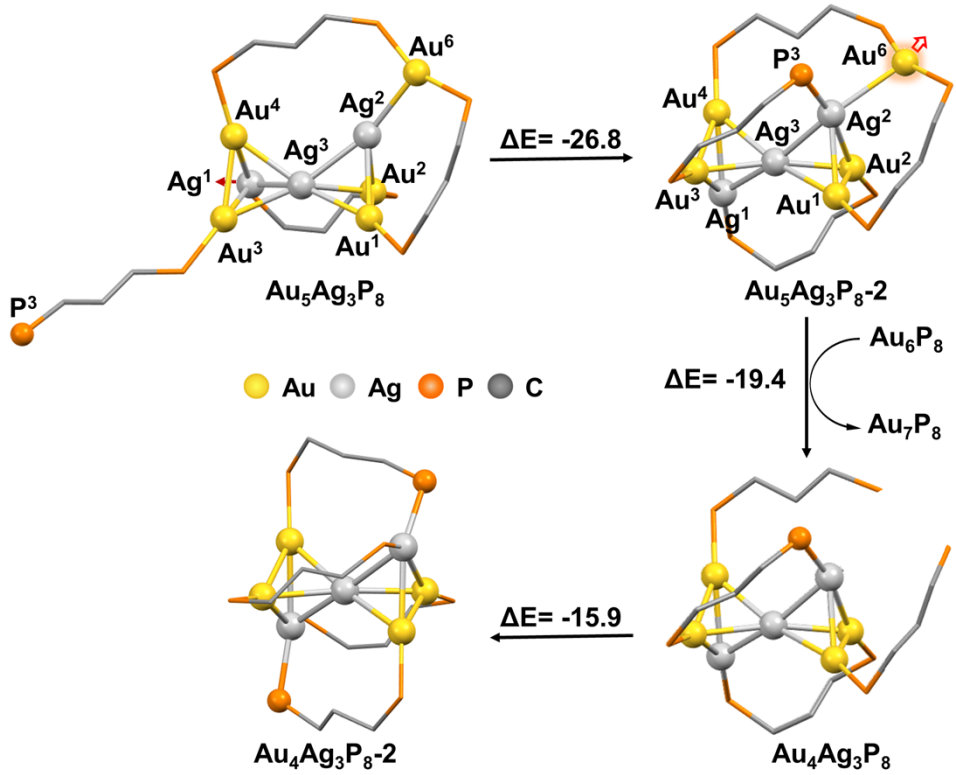


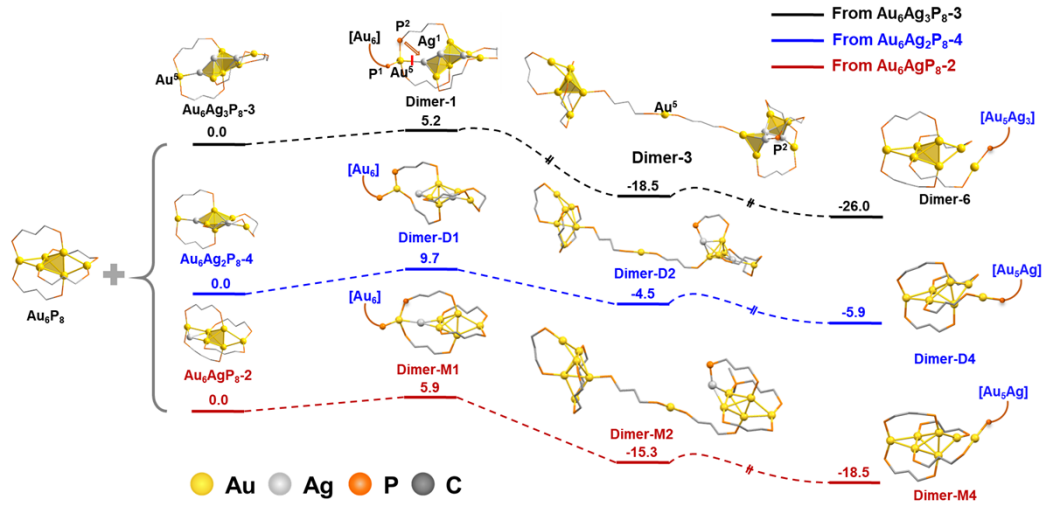
Figure S9. The energy profile for the Au-Au formation from **Dimer-6** to **Dimer-7**. The remained part of **Dimer-6** was omitted. Each restricted optimization was performed with the fixed bond length of $Au^{4'}$-Au^{5}.



Scheme S3. The comparison between reactions of $\mathbf{Au_6Ag_3P_8}$**-3** + $\mathbf{Au_6P_8}$ → $\mathbf{Au_7P_8}$ + $\mathbf{Au_5Ag_3P_8}$ and $\mathbf{Au_6Ag_3P_8}$**-3** + $\mathbf{Au_6P_8}$ → $\mathbf{Au_6AgP_8}$ + $\mathbf{Au_6Ag_2P_8}$.



Scheme S4. The reaction from **$Au_5Ag_3P_8$** to **$Au_5Ag_3P_8$-2** and the possible further size-conversion.



Scheme S5. The possible pathways of size-growth from **$Au_6Ag_3P_8$-3**, **$Au_6Ag_2P_8$-4**, and **Au_6AgP_8-2**. The independent **Au_6P_8** and each Au_6Ag_n species were set as the reference for each pathway.