Electronic Supplementary Material (ESI) for Chemical Science.
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Supporting Information:

Stability Enhancement Factor beyond Eight-Electron Shell Closure in Thiacalix[4]arene-Protected Silver Clusters

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I. Characterization

Figure.

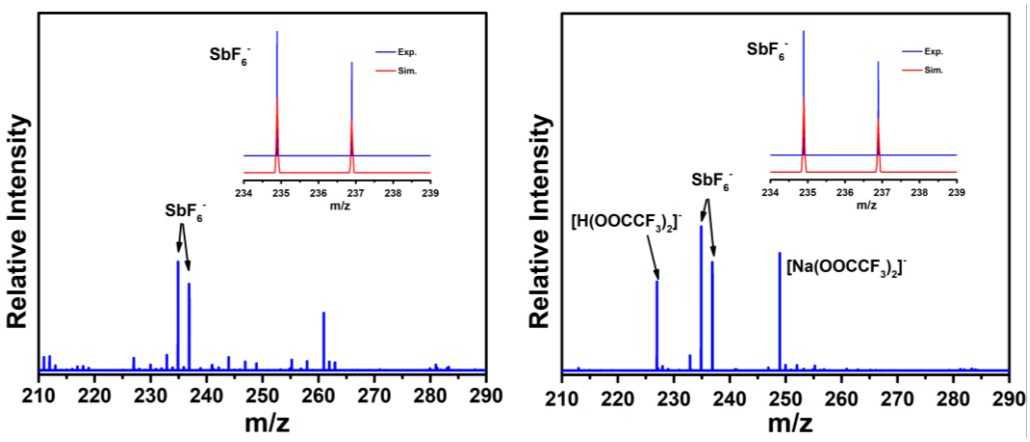

Fig. S1. Negative ion mode ESI-MS of cluster **1** (left) and cluster **2** (right).

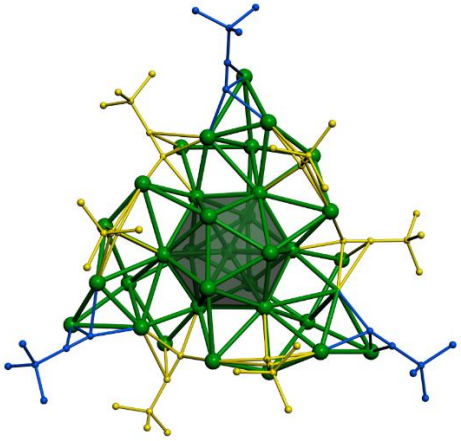

Fig. S2. The coordination modes of alkynyl ligands in cluster **1**.

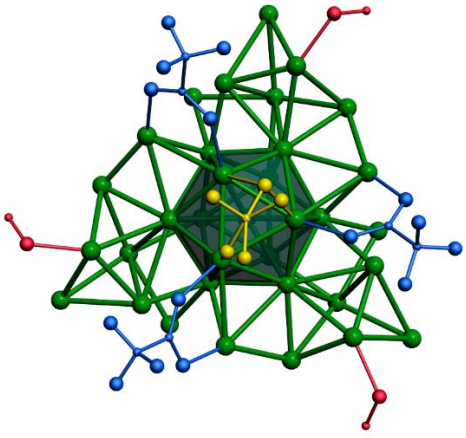

Fig. S3. The coordination modes of trifluoroacetic acid ligands and Methanol in cluster **1**.

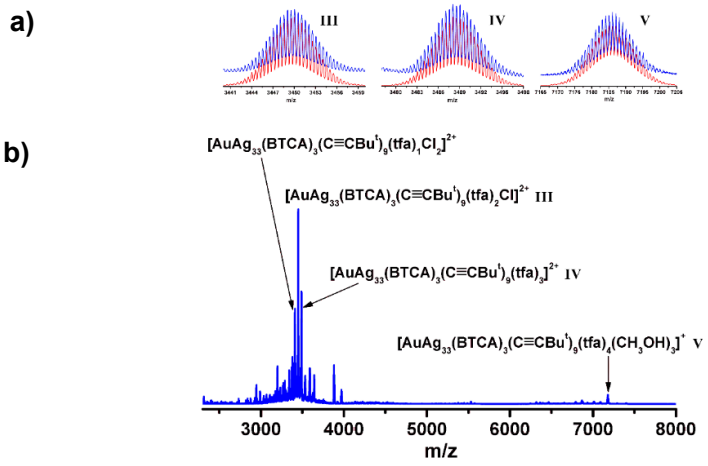

Fig. S4. (a) The measured (blue trace) and simulated (red trace) isotopic patterns of $[AuAg_{33}(BTCA)_3(C{\equiv}CBu^t)_9(tfa)_2Cl_1]^{2+}$ (III), $[AuAg_{33}(BTCA)_3(C{\equiv}CBu^t)_9(tfa)_3]^{2+}$ (IV) and $[AuAg_{33}(BTCA)_3(C{\equiv}CBu^t)_9(tfa)_4(CH_3OH)_3]^{+}$ (V). (b) Mass spectrum of the cluster **2**.

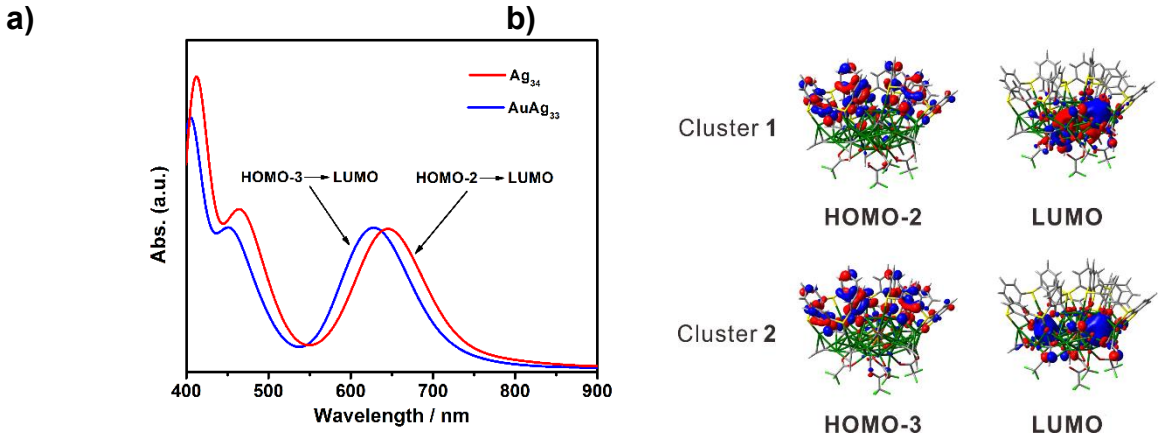

Fig. S5. (a) TDDFT optical absorption spectrum of $[Ag_{34}(TCA)_3(C{\equiv}CH)_9(tfa)_4]^{+}$ (red) and $[AuAg_{33}(TCA)_3(C{\equiv}CH)_9(tfa)_4]^{+}$ (blue). (b) The molecular orbitals of cluster **1** and cluster **2**.

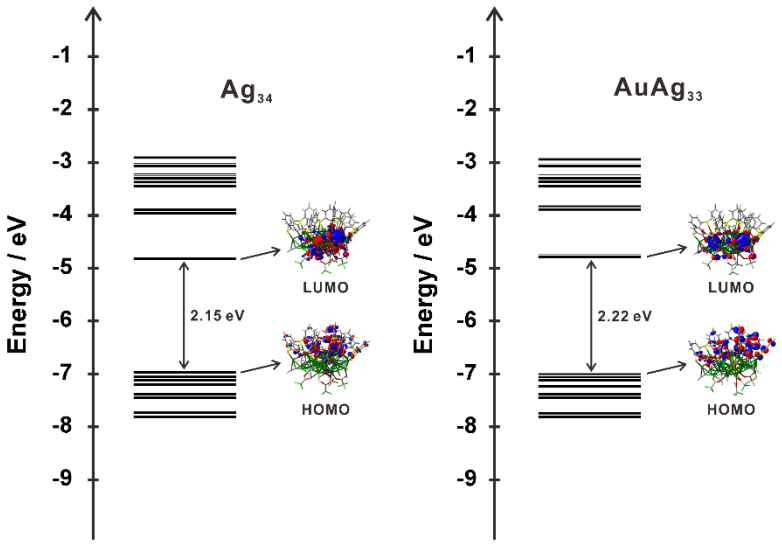

Fig. S6. The Kohn–Sham orbital energy levels and the electronic diagrams of HOMO, LUMO of $[Ag_{34}(TCA)_3(C{\equiv}CH)_9(tfa)_4]^{+}$ and $[AuAg_{33}(TCA)_3(C{\equiv}CH)_9(tfa)_4]^{+}$.

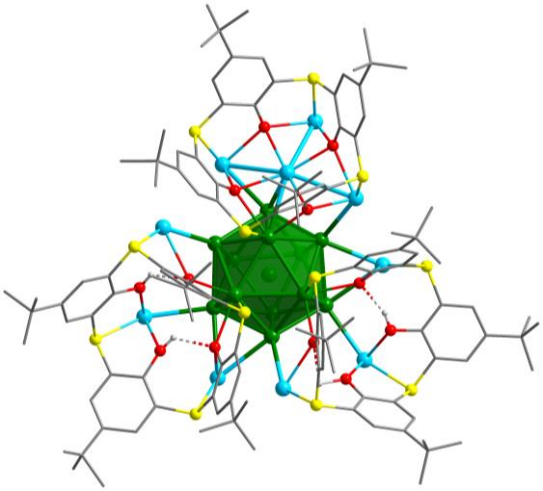

Fig. S7. The coordination motif of the thiacalix[4]arene in Ag_{35}.

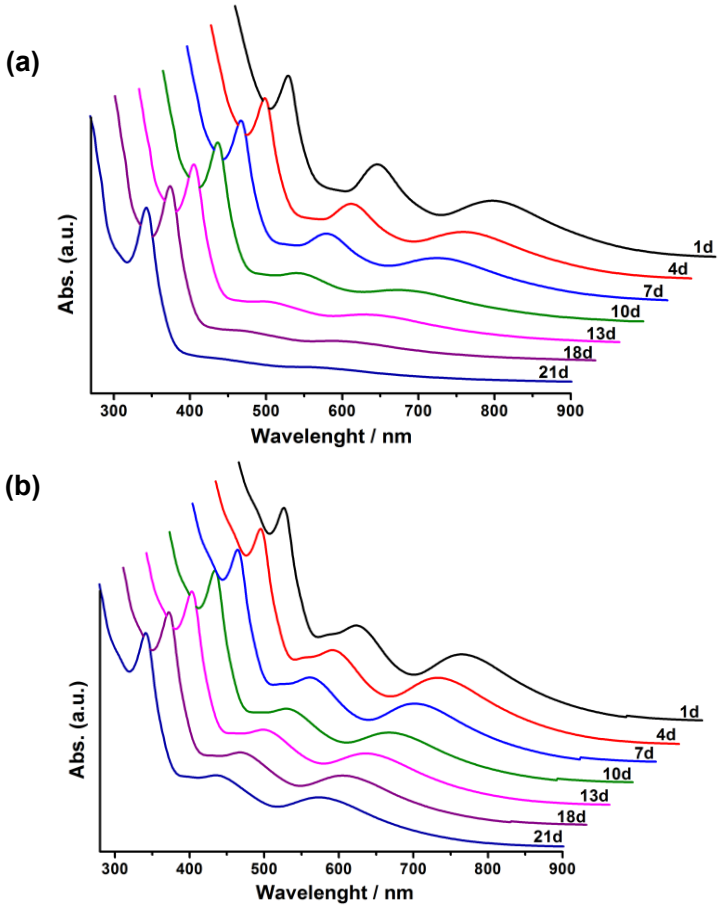

Fig. S8. UV-vis spectra of cluster **1** (a) and **2** (b) measured at different time for stability check (CH_2Cl_2 solution under the light).

Table S1. Interaction energy between the central atom and Ag_{12} shell in cluster **1** and **2**.

	Energy (a.u.)	Energy (kJ/mol)
Interaction energy between Ag and Ag_{12} shell in cluster **1**	0.67	1759.08
Interaction energy between Au and Ag_{12} shell in cluster **2**	0.6745	1770.90