Supporting Information

Extensive Polymerization of Atomically Precise Alloy Metal Clusters During Solid State Reactions

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1. Experimental section

Synthesis of $HAuCl_4.3H_2O$

A 24 karat gold coin, weighing 2 g, was taken in a round bottom flask and added 10 ml of conc. HCl into it. Then it was heated at 60°C for 5 minutes. Into the hot solution, 4 ml of conc. HNO_3 was added dropwise, and bubble formation was observed. Continue the addition of HNO_3 until the bubbles are not formed. The solution was heated until the gold dissolves completely. After the complete dissolution of gold, the solution was cooled down to room temperature. Then it is further cooled at 0°C for 24 h, to precipitate out the impurities. The precipitate were removed by filtration, and 5 ml of distilled water was added to the filtrate. Further the filtrate was kept for slow evaporation, in presence of the drying agent phosphorus pentaoxide, to get the crystalline product $HAuCl_4.3H_2O$.

2. Instrumentation

UV-Vis absorption spectra of the cluster in their respective solution were optimized using a PerkinElmer Lambda 25 spectrophotometer in the 200–1100 nm wavelength range. The slit width used for the measurement is 1 nm.

Mass spectra of all the clusters were measured using Waters Synapt G2Si HDMS instrument. The instrument is equipped with an electrospray ionization source, mass selected ion trap, ion mobility cells, and time of flight mass analyzer. All MS measurements were acquired in the negative ion mode. An optimized operating conditions such as flow rate 15-20 μL/min, capillary voltage 2-3 kV, cone voltage 20 V, source offset 10 V, desolvation gas flow 400 L/min and source temperature 80-100 °C were used for the measurements.

The interaction between the clusters lead to the formation of multiple polymeric species as observed in ESI-MS (see **Figure 1, 2**), making it difficult to assign charge states in the case of metal-exchanged alloy clusters and their polymeric entities, especially when isotopic resolution is lacking and charge states overlap within complex mass spectra. Experimentally acquired ESI MS spectra were analyzed using UniDec software to address these challenges.[1] This approach allowed for a clearer visualization of the relative intensities of cluster ions, including the less intense polymer ions, in a ‘Heat map’ plot, and helped to reduce mass uncertainty in the spectrum.

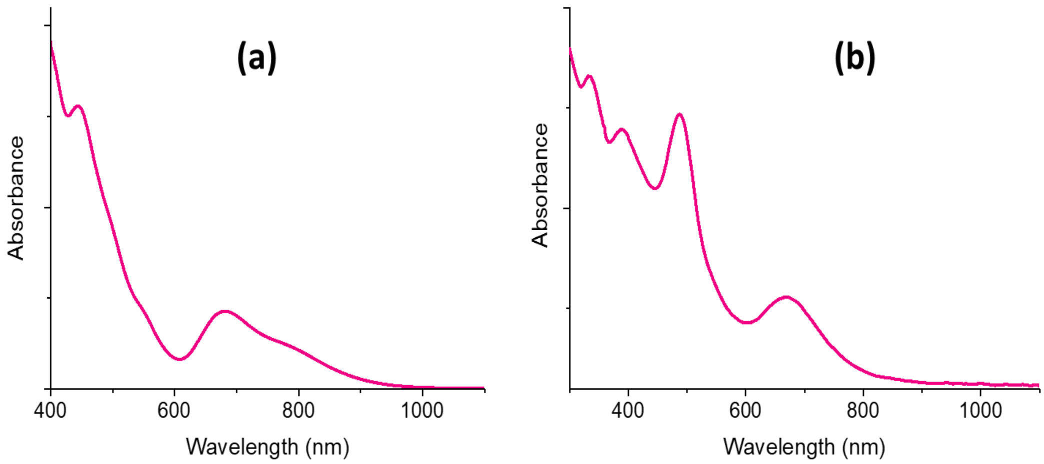

Figure S1. UV-Vis absorption spectra of (a) $[Au_{25}(PET)_{18}]^-$, and (b) $[Ag_{25}(DMBT)_{18}]^-$ clusters in acetonitrile solvent.

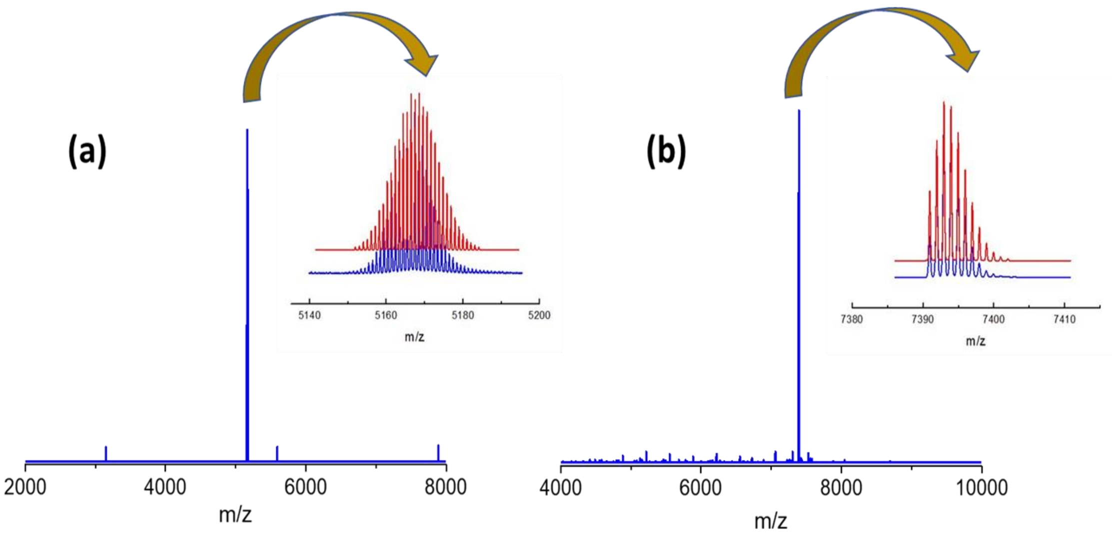

Figure S2. ESI-MS of (a) $[Ag_{25}(DMBT)_{18}]^-$, and (b) $[Au_{25}(PET)_{18}]^-$ cluster, measured in acetonitrile solvent.

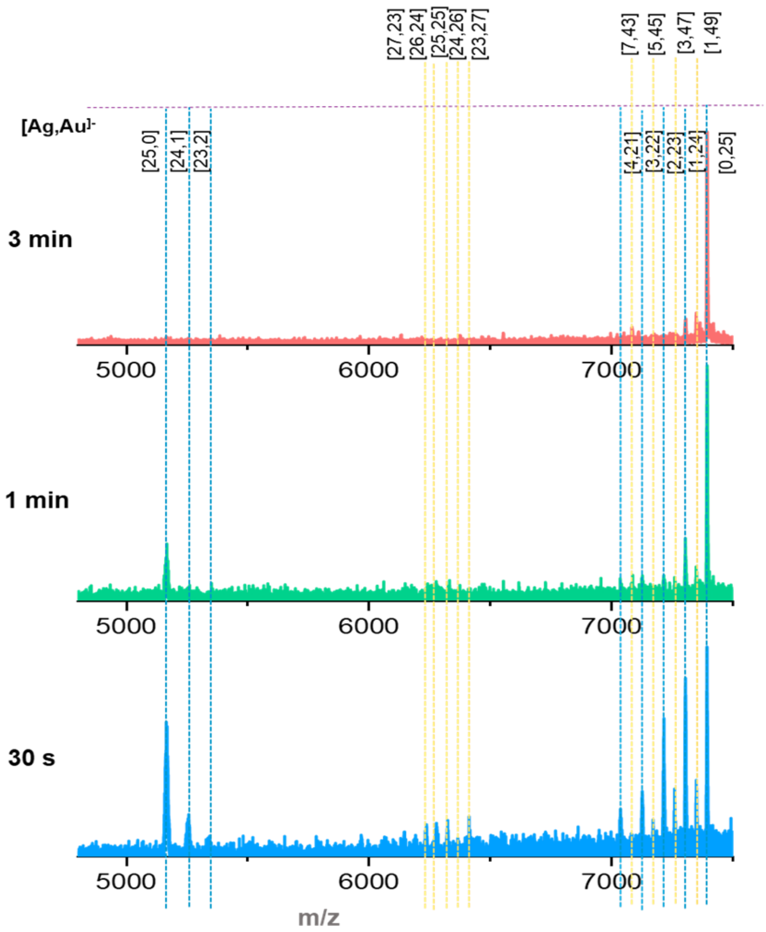

Figure S3. Time-dependent ESI-MS, after grinding 1:3 mixture of $Ag_{25}(SR)_{18}$:$Au_{25}(SR)_{18}$, in the solid state.

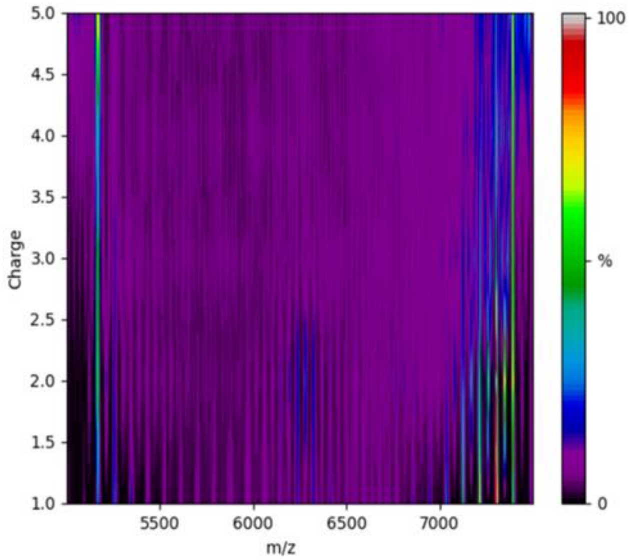

Figure S4. Heat map plot obtained from the mass spectra of grinding 1:3 mixture of $Ag_{25}(SR)_{18}$:$Au_{25}(SR)_{18}$, in the solid state.

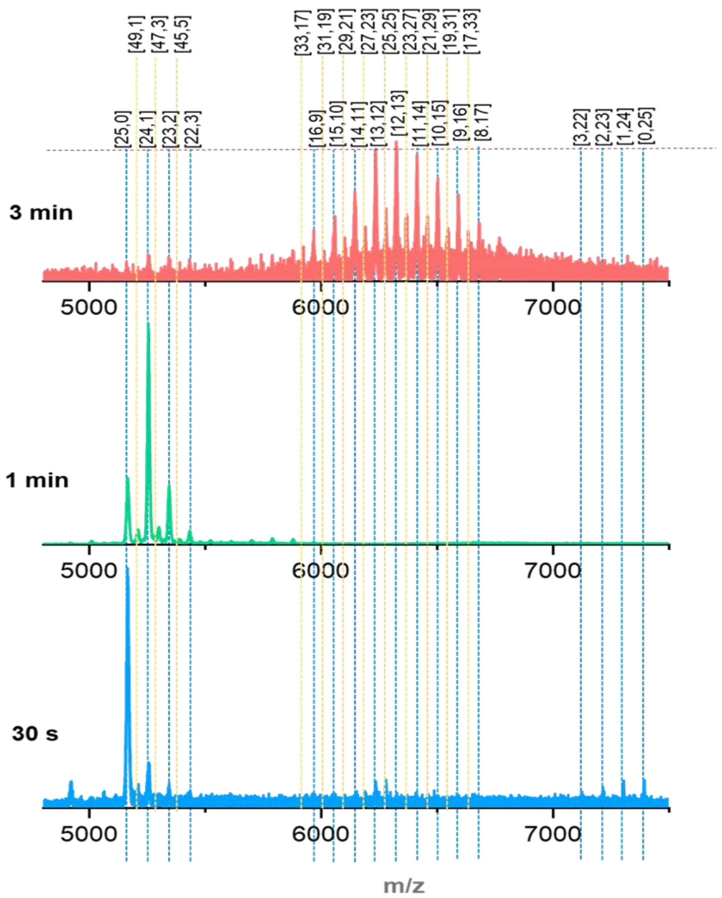

Figure S5. Time-dependent ESI-MS, after grinding 3:1 mixture of $Ag_{25}(SR)_{18}$:$Au_{25}(SR)_{18,}$ in the solid state.

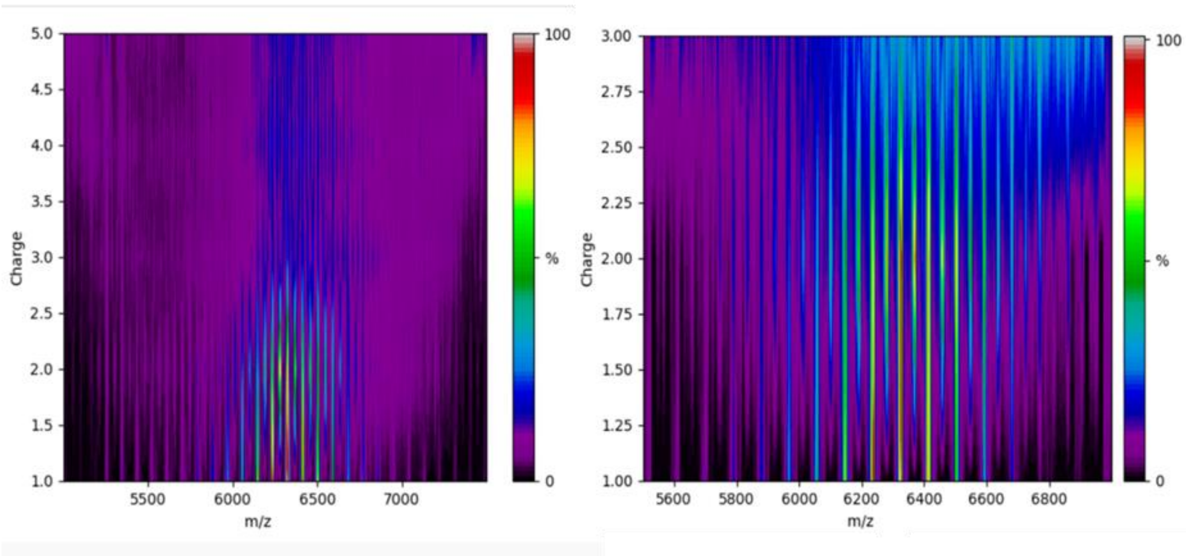

Figure S6. Heat map plot obtained from the mass spectra of grinding 3:1 mixture of $Ag_{25}(SR)_{18}$:$Au_{25}(SR)_{18,}$ in the solid state.

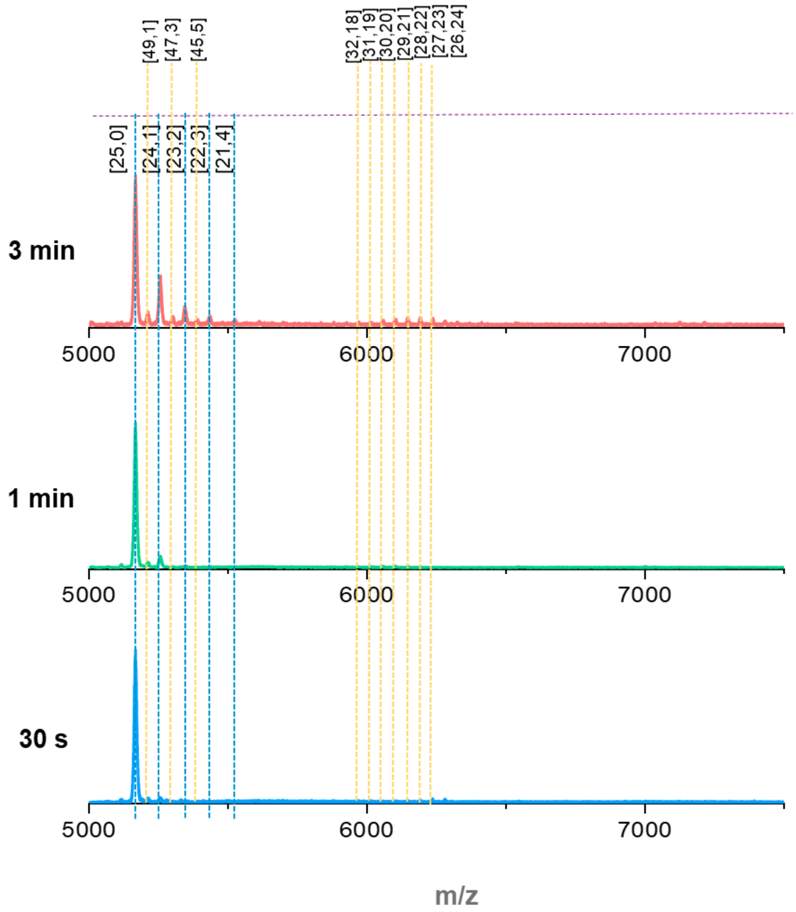

Figure S7. Time-dependent ESI-MS, after grinding 1:5 mixture of $Ag_{25}(SR)_{18}$:$Au_{25}(SR)_{18}$, in the solid state.

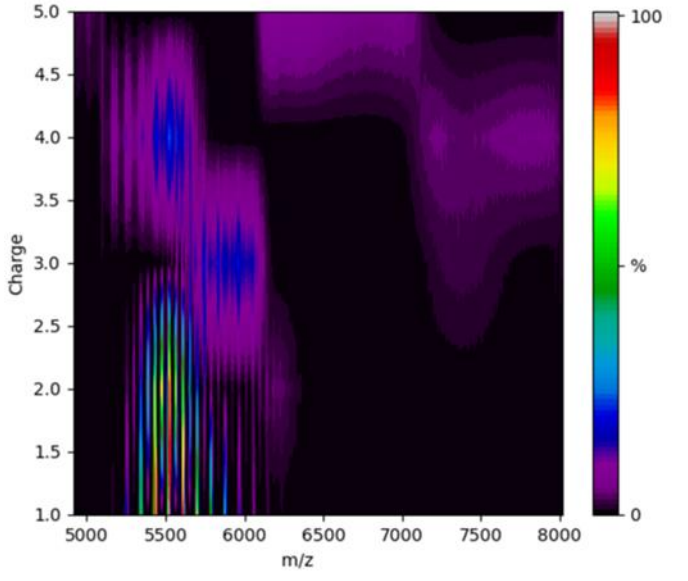

Figure S8. Heat map plot obtained from the mass spectra of grinding 1:5 mixture of $Ag_{25}(SR)_{18}$:$Au_{25}(SR)_{18}$, in the solid state.

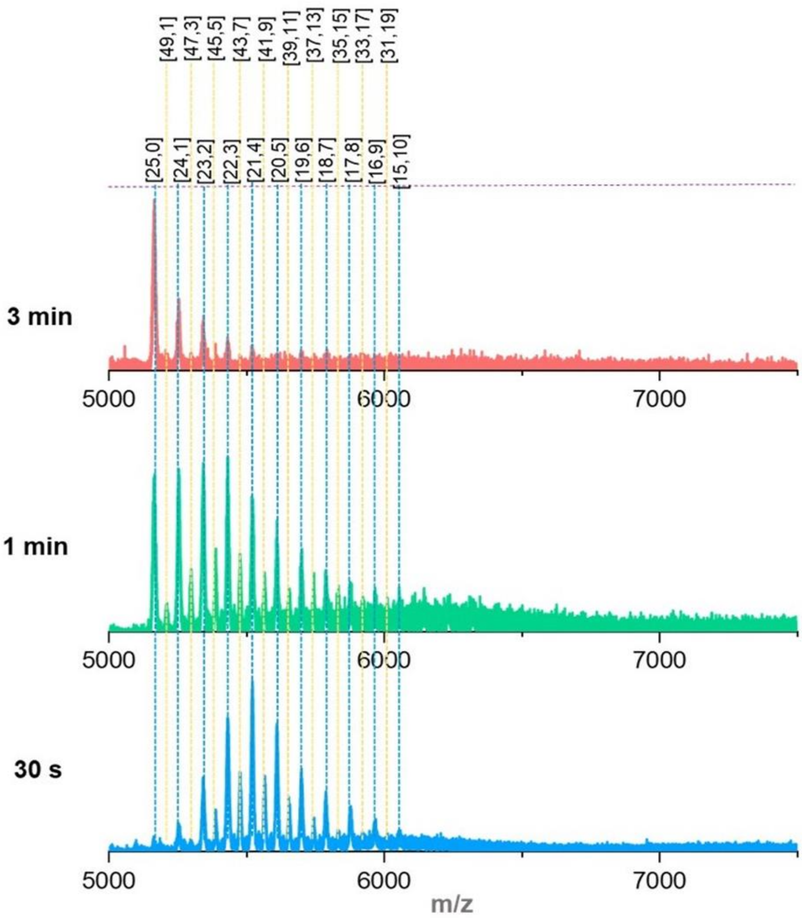

Figure S9. Time-dependent ESI-MS, after grinding a 5:1 mixture of $Ag_{25}(SR)_{18}$:$Au_{25}(SR)_{18}$ in the solid state.

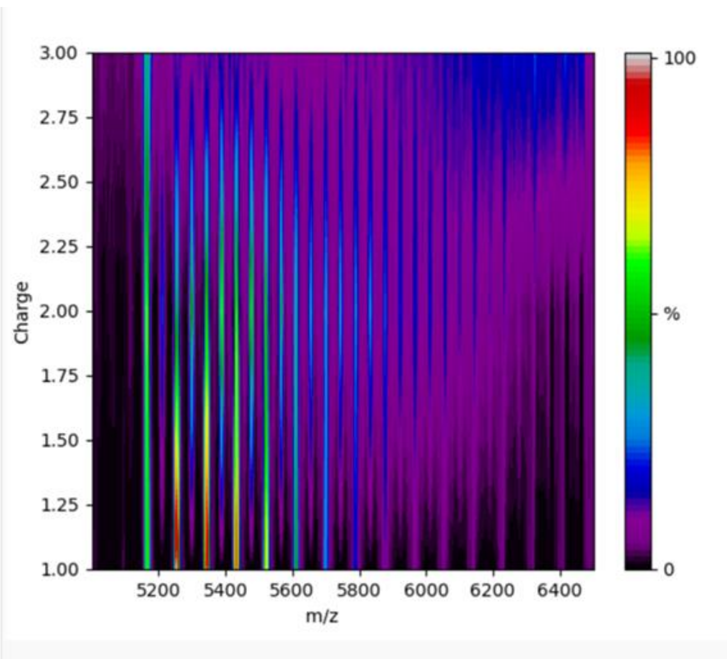

Figure S10. Heat map plot obtained from the mass spectra, of grinding 5:1 mixture of $Ag_{25}(SR)_{18}$:$Au_{25}(SR)_{18,}$ in the solid state.

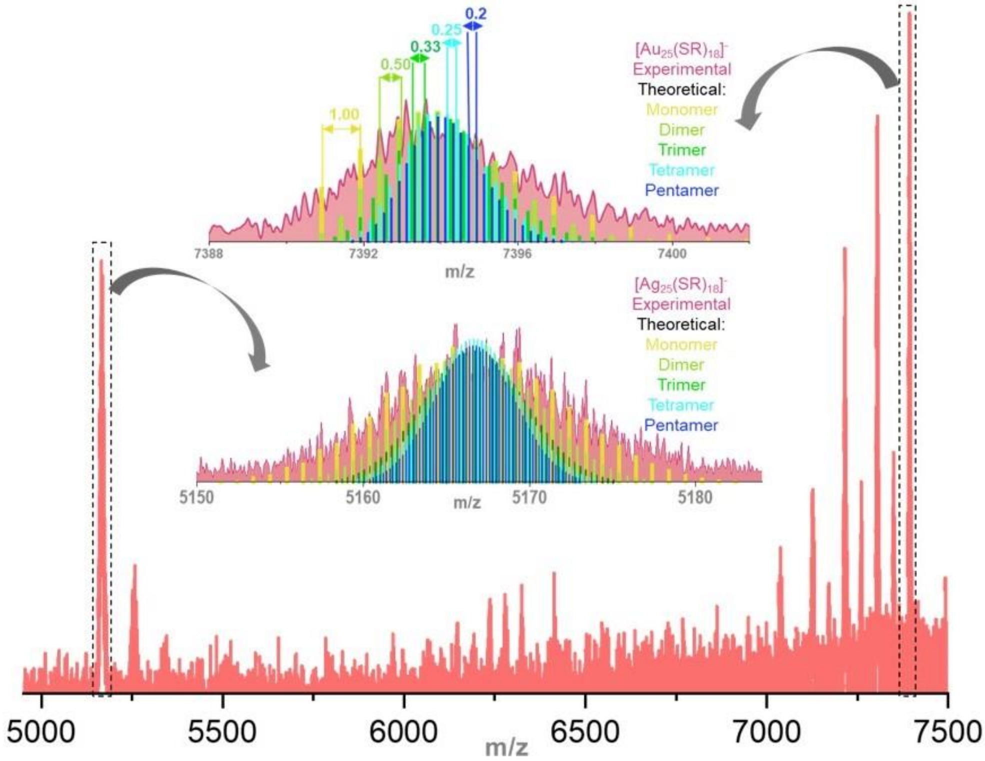

Figure S11. ESI-MS showing various homopolymers of $Au_{25}(SR)_{18}$ at m/z 7393, i.e., $[Au_{125}(SR)_{90}]^{5-}$, $[Au_{100}(SR)_{72}]^{4-}$, $[Au_{75}(SR)_{54}]^{3-}$, and $[Au_{50}(SR)_{25}]^{2-}$, and $Ag_{25}(SR)_{18}$ at m/z 5167, i.e., $[Ag_{125}(SR)_{90}]^{5-}$, $[Ag_{100}(SR)_{72}]^{4-}$, $[Ag_{75}(SR)_{54}]^{3-}$, and $[Ag_{50}(SR)_{25}]^{2-}$.

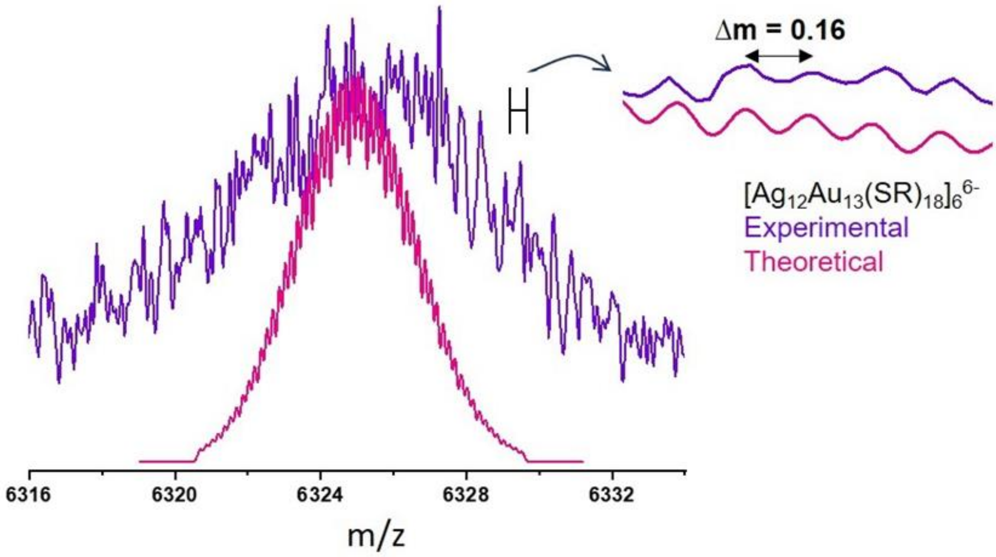

Figure S12. ESI-MS of the hexamer species $[Ag_{72}Au_{78}(SR)_{108}]^{6-}$, along with its theoretical fitting. The instrumental resolution was poor at high mas range to clearly resolve all the peaks.

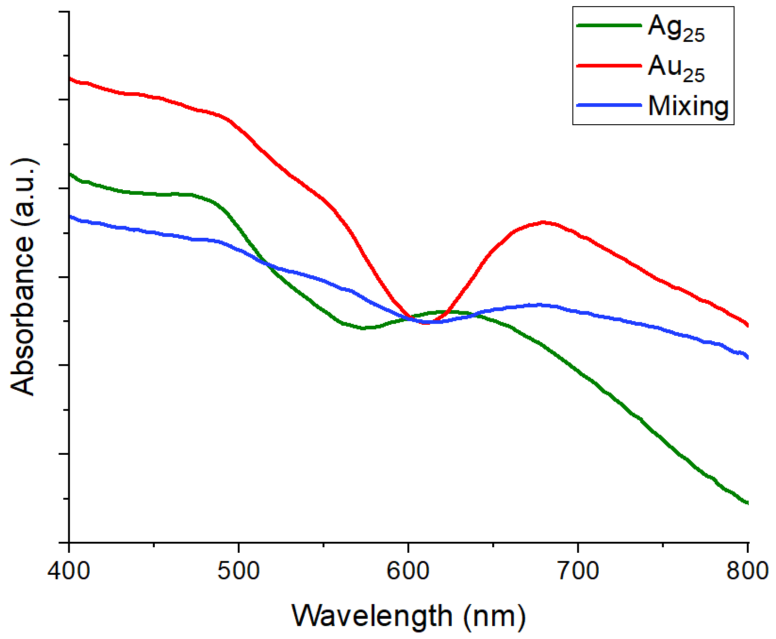

Figure S13. Solid state UV-Vis absorption spectra upon mixing the clusters in the solid state. Due to the limitation of the instrument, we could not measure the spectra above 800 nm.

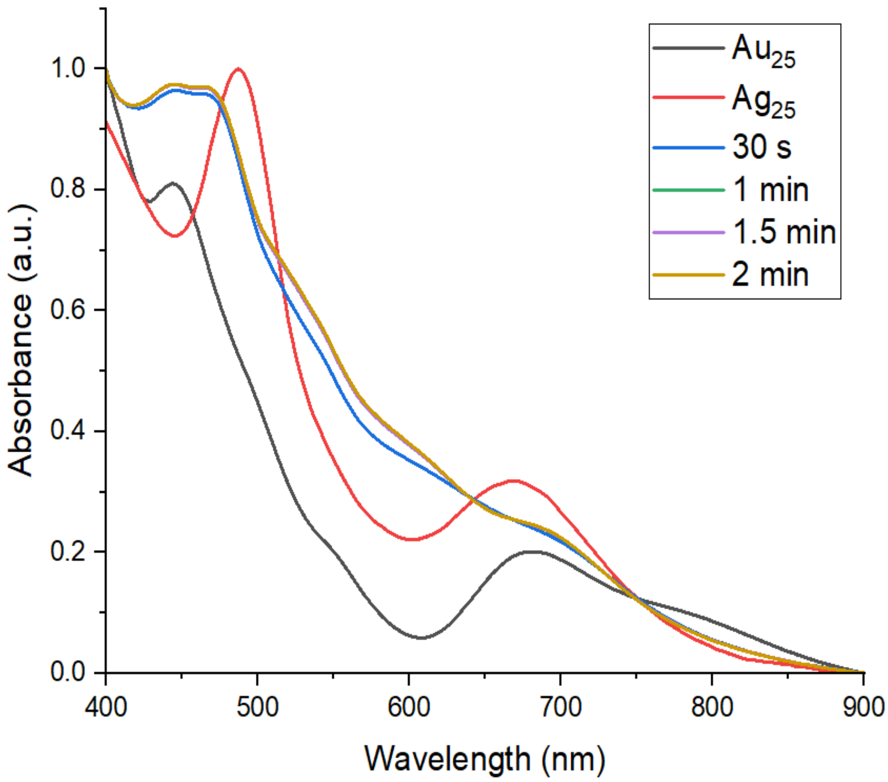

Figure S14. The time-dependent UV-Vis absorption spectra measured by dissolving the ground mixture in cold acetonitrile.

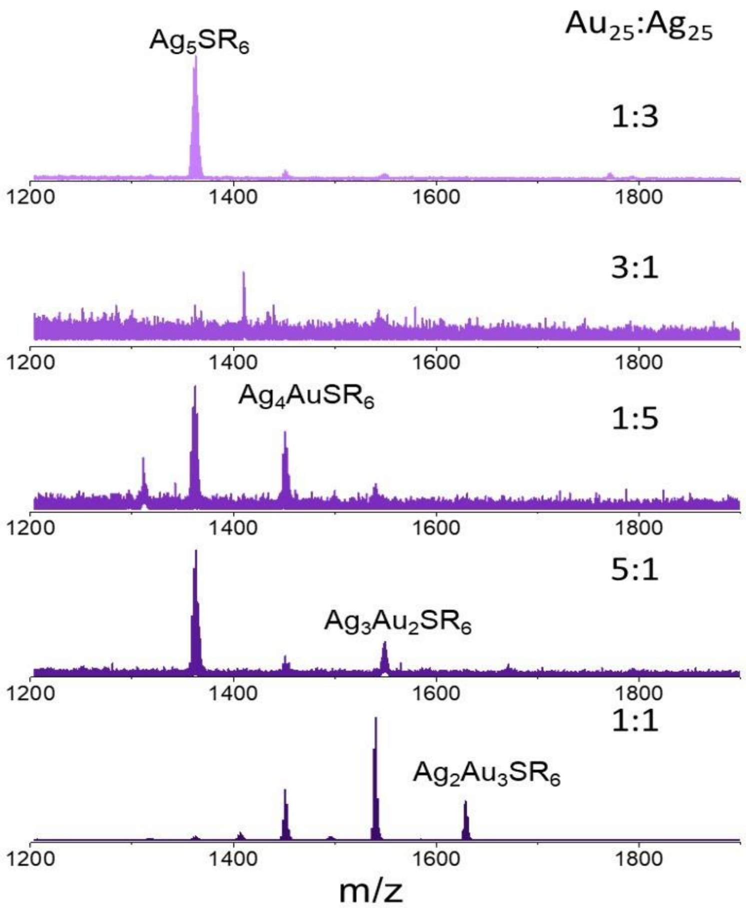

Figure S15. The degradation peaks after the reaction, for different ratios of $Ag_{25}(SR)_{18}$ and $Au_{25}(SR)_{18}$.

Table S1. The detailed information of all the polymeric species observed in mass spectrometry studies of 1:1 $Ag_{25}(SR)_{18}$:$Au_{25}(SR)_{18}$.

m/z	Monomers	m/z	Dimers	m/z	Trimers	m/z	Tetramers
7393	$Au_{25}(SR)_{18}$	7350	$AgAu_{24}(SR)_{18}$ + $Au_{25}(SR)_{18}$			5545	$Ag_{83}Au_{17}(SR)_{72}$
7305	$AgAu_{24}(SR)_{18}$	7308	2[$AgAu_{24}(SR)_{18}$]			5590	$Ag_{81}Au_{19}(SR)_{72}$
7216	$Ag_2Au_{23}(SR)_{18}$	7260	$AgAu_{24}(SR)_{18}$ + $Ag_2Au_{23}(SR)_{18}$			5634	$Ag_{79}Au_{21}(SR)_{72}$
7127	$Ag_3Au_{22}(SR)_{18}$	7172	$Ag_3Au_{22}(SR)_{18}$ + $Ag_2Au_{23}(SR)_{18}$			5679	$Ag_{77}Au_{23}(SR)_{72}$

Table S2. The detailed information of all the polymeric species observed in mass spectrometry studies of 1:3 $Ag_{25}(SR)_{18}$: $Au_{25}(SR)_{18}$.

m/z	Monomers	m/z	Dimers	m/z	Trimers	m/z	Tetramers
5167	$Ag_{25}(SR)_{18}$	6280	$Au_{25}Ag_{25}(SR)_{36}$	5167	$3[Ag_{25}(SR)_{18}]$	5167	$4[Ag_{25}(SR)_{18}]$
5256	$AuAg_{24}(SR)_{18}$	6235	$Au_{24}Ag_{26}(SR)_{36}$	7216	$3[Ag_2Au_{23}(SR)_{18}]$	7393	$4[Au_{25}(SR)_{18}]$
5345	$Au_2Ag_{23}(SR)_{18}$	6324	$Au_{26}Ag_{24}(SR)_{36}$	7305	$3[AgAu_{24}(SR)_{18}]$		
5434	$Au_3Ag_{22}(SR)_{18}$	6189	$Au_{23}Ag_{27}(SR)_{36}$	7393	$3[Au_{25}(SR)_{18}]$		
5702	$Au_6Ag_{19}(SR)_{18}$	6144	$Au_{22}Ag_{28}(SR)_{36}$				
5792	$Au_7Ag_{18}(SR)_{18}$	6100	$Au_{21}Ag_{29}(SR)_{36}$				
5970	$Au_9Ag_{16}(SR)_{18}$	6369	$Au_{27}Ag_{23}(SR)_{36}$				
		6414	$Au_{28}Ag_{22}(SR)_{36}$				
		6459	$Au_{29}Ag_{21}(SR)_{36}$				

Table S3. The detailed information of all the polymeric species observed in mass spectrometry studies of 3:1 $Ag_{25}(SR)_{18}$: $Au_{25}(SR)_{18}$.

m/z	Monomers	m/z	Dimers	m/z	Trimers	m/z	Tetramers
6324	$Ag_{12}Au_{13}(SR)_{18}$	6324	$2[Ag_{12}Au_{13}(SR)_{18}]$	6324	$3[Ag_{12}Au_{13}(SR)_{18}]$	6324	$4[Ag_{12}Au_{13}(SR)_{18}]$
6413	$Ag_{11}Au_{14}(SR)_{18}$	6370	$Ag_{12}Au_{13}(SR)_{18}$ + $Ag_{11}Au_{14}(SR)_{18}$	6413	$3[Ag_{11}Au_{14}(SR)_{18}]$	6347	$3[Ag_{12}Au_{13}(SR)_{18}]$ + $Ag_{11}Au_{14}(SR)_{18}$
6504	$Ag_{10}Au_{15}(SR)_{18}$	6413	$Ag_{11}Au_{14}(SR)_{18}$ + $Ag_{11}Au_{14}(SR)_{18}$	6264	$2[Ag_{13}Au_{12}(SR)_{18}]$ + $Ag_{12}Au_{13}(SR)_{18}$	6390	$3[Ag_{11}Au_{14}(SR)_{18}]$ + $Ag_{12}Au_{13}(SR)_{18}$
6593	$Ag_9Au_{16}(SR)_{18}$	6459	$Ag_{11}Au_{14}(SR)_{18}$ + $Ag_{10}Au_{15}(SR)_{18}$	6354	$2[Ag_{12}Au_{13}(SR)_{18}]$ + $Ag_{11}Au_{14}(SR)_{18}$	6436	$3[Ag_{11}Au_{14}(SR)_{18}]$ + $Ag_{10}Au_{15}(SR)_{18}$
6683	$Ag_8Au_{17}(SR)_{18}$	6549	$Ag_{10}Au_{15}(SR)_{18}$ + $Ag_9Au_{16}(SR)_{18}$	6384	$2[Ag_{11}Au_{14}(SR)_{18}]$ + $Ag_{12}Au_{13}(SR)_{18}$	6480	$3[Ag_{10}Au_{15}(SR)_{18}]$ + $Ag_{11}Au_{14}(SR)_{18}$
6771	$Ag_7Au_{18}(SR)_{18}$	6638	$Ag_9Au_{16}(SR)_{18}$ + $Ag_8Au_{17}(SR)_{18}$	6472	$2[Ag_{10}Au_{15}(SR)_{18}]$ + $Ag_{11}Au_{14}(SR)_{18}$	6256	$3[Ag_{13}Au_{12}(SR)_{18}]$ + $Ag_{12}Au_{11}(SR)_{18}$
6860	$Ag_6Au_{19}(SR)_{18}$	6683	$Ag_8Au_{17}(SR)_{18}$ + $Ag_8Au_{17}(SR)_{18}$	6530	$2[Ag_{10}Au_{15}(SR)_{18}]$ + $Ag_9Au_{16}(SR)_{18}$	6213	$3[Ag_{13}Au_{12}(SR)_{18}]$ + $Ag_{14}Au_{11}(SR)_{18}$
6145	$Ag_{14}Au_{11}(SR)_{18}$	6771	$Ag_7Au_{18}(SR)_{18}$ + $Ag_7Au_{18}(SR)_{18}$	6204	$2[Ag_{13}Au_{12}(SR)_{18}]$ + $Ag_{14}Au_{11}(SR)_{18}$	6168	$3[Ag_{14}Au_{11}(SR)_{18}]$ + $Ag_{13}Au_{12}(SR)_{18}$
6234	$Ag_{13}Au_{12}(SR)_{18}$	6817	$Ag_6Au_{19}(SR)_{18}$ + $Ag_7Au_{18}(SR)_{18}$	6176	$2[Ag_{14}Au_{11}(SR)_{18}]$ + $Ag_{13}Au_{12}(SR)_{18}$	6123	$3[Ag_{14}Au_{11}(SR)_{18}]$ + $Ag_{15}Au_{10}(SR)_{18}$
6056	$Ag_{15}Au_{10}(SR)_{18}$	6861	$Ag_6Au_{19}(SR)_{18}$ + $Ag_6Au_{19}(SR)_{18}$	6114	$2[Ag_{14}Au_{11}(SR)_{18}]$ + $Ag_{15}Au_{10}(SR)_{18}$	6079	$3[Ag_{15}Au_{10}(SR)_{18}]$ + $Ag_{14}Au_{11}(SR)_{18}$
5967	$Ag_{16}Au_9(SR)_{18}$	6145	$Ag_{14}Au_{11}(SR)_{18}$ + $Ag_{14}Au_{11}(SR)_{18}$				
5878	$Ag_{17}Au_8(SR)_{18}$	6189	$Ag_{14}Au_{11}(SR)_{18}$ + $Ag_{13}Au_{12}(SR)_{18}$				

5790	$Ag_{18}Au_7(SR)_{18}$	6234	$Ag_{13}Au_{12}(SR)_{18}$ + $Ag_{13}Au_{12}(SR)_{18}$				
		6279	$Ag_{13}Au_{12}(SR)_{18}$ + $Ag_{12}Au_{13}(SR)_{18}$				
		6324	$Ag_{12}Au_{13}(SR)_{18}$ + $Ag_{12}Au_{13}(SR)_{18}$				
		6102	$Ag_{14}Au_{11}(SR)_{18}$ + $Ag_{15}Au_{10}(SR)_{18}$				
		6011	$Ag_{15}Au_{10}(SR)_{18}$ + $Ag_{16}Au_9(SR)_{18}$				
		5967	$Ag_{16}Au_9(SR)_{18}$ + $Ag_{16}Au_9(SR)_{18}$				
		5922	$Ag_{16}Au_9(SR)_{18}$ + $Ag_{17}Au_8(SR)_{18}$				
		5878	$Ag_{17}Au_8(SR)_{18}$ + $Ag_{17}Au_8(SR)_{18}$				
		5833	$Ag_{18}Au_7(SR)_{18}$ + $Ag_{17}Au_8(SR)_{18}$				
		5790	2[$Ag_{18}Au_7(SR)_{18}$]				

Table S4. The detailed information of all the polymeric species observed in mass spectrometry studies of 1:5 $Ag_{25}(SR)_{18}$: $Au_{25}(SR)_{18}$.

m/z	Monomers	m/z	Dimers	m/z	Trimers	m/z	Tetramers
5167	$Ag_{25}(SR)_{18}$	5212	$AuAg_{49}(SR)_{36}$	5227	$AuAg_{49}(SR)_{36}$ + $AuAg_{24}(SR)_{18}$	5278	3[$AuAg_{24}(SR)_{18}$] + [$Au_2Ag_{23}(SR)_{18}$]
5256	$AuAg_{24}(SR)_{18}$	5300	$Au_3Ag_{47}(SR)_{36}$			5323	3[$Au_2Ag_{23}(SR)_{18}$] + [$AuAg_{24}(SR)_{18}$]
5345	$Au_2Ag_{23}(SR)_{18}$	5390	$Au_5Ag_{45}(SR)_{36}$			5367	3[$Au_2Ag_{23}(SR)_{18}$] + [$Au_3Ag_{22}(SR)_{18}$]
5434	$Au_3Ag_{22}(SR)_{18}$	5480	$Au_7Ag_{43}(SR)_{36}$			5412	3[$Au_3Ag_{22}(SR)_{18}$] + [$Au_2Ag_{23}(SR)_{18}$]
5523	$Au_4Ag_{21}(SR)_{18}$	5968	$Au_{18}Ag_{32}(SR)_{36}$			5501	3[$Au_4Ag_{21}(SR)_{18}$] + [$Au_3Ag_{22}(SR)_{18}$]
5612	$Au_5Ag_{20}(SR)_{18}$	6013	$Au_{19}Ag_{31}(SR)_{36}$			6080	$Au_{21}Ag_{29}(SR)_{36}$ + $Au_{20}Ag_{30}(SR)_{36}$
		6058	$Au_{20}Ag_{30}(SR)_{36}$			6125	$Au_{21}Ag_{29}(SR)_{36}$ + $Au_{22}Ag_{28}(SR)_{36}$
		6102	$Au_{21}Ag_{29}(SR)_{36}$			6169	$Au_{22}Ag_{28}(SR)_{36}$ + $Au_{23}Ag_{27}(SR)_{36}$
		6147	$Au_{22}Ag_{28}(SR)_{36}$			6213	$Au_{23}Ag_{27}(SR)_{36}$ + $Au_{24}Ag_{26}(SR)_{36}$
		6191	$Au_{23}Ag_{27}(SR)_{36}$			6258	$Au_{25}Ag_{25}(SR)_{36}$ +

							$Au_{24}Ag_{26}(SR)_{36}$
		6236	$Au_{24}Ag_{26}(SR)_{36}$			6303	$Au_{25}Ag_{25}(SR)_{36}$ + $Au_{26}Ag_{24}(SR)_{36}$
		6280	$Au_{25}Ag_{25}(SR)_{36}$				
		6325	$Au_{26}Ag_{24}(SR)_{36}$				
		6369	$Au_{27}Ag_{23}(SR)_{36}$				

Table S5. The detailed information of all the polymeric species observed in mass spectrometry studies of 5:1 $Ag_{25}(SR)_{18}$: $Au_{25}(SR)_{18}$.

m/z	Monomers	m/z	Dimers	m/z	Trimers	m/z	Tetramers
5167	$Ag_{25}(SR)_{18}$	5211	$Ag_{25}(SR)_{18}$ + $AuAg_{24}(SR)_{18}$	5285	[$AuAg_{24}(SR)_{18}$] + [$Au_3Ag_{47}(SR)_{36}$]	5322	[$Au_3Ag_{47}(SR)_{36}$] + [$Au_4Ag_{46}(SR)_{36}$]
5256	$AuAg_{24}(SR)_{18}$	5300	$AuAg_{24}(SR)_{18}$ + $Au_2Ag_{23}(SR)_{18}$	5344	[$Au_3Ag_{22}(SR)_{18}$] + [$Au_3Ag_{47}(SR)_{36}$]	5410	[$Au_5Ag_{45}(SR)_{36}$] + [$Au_6Ag_{44}(SR)_{36}$]
5344	$Au_2Ag_{23}(SR)_{18}$	5388	$Au_2Ag_{23}(SR)_{18}$ + $Au_3Ag_{22}(SR)_{18}$	5373	[$Au_2Ag_{23}(SR)_{18}$] + [$Au_5Ag_{45}(SR)_{36}$]		
5432	$Au_3Ag_{22}(SR)_{18}$	5477	$Au_3Ag_{22}(SR)_{18}$ + $Au_4Ag_{21}(SR)_{18}$	5432	[$Au_4Ag_{21}(SR)_{18}$] + [$Au_5Ag_{45}(SR)_{36}$]		
5521	$Au_4Ag_{21}(SR)_{18}$	5566	$Au_4Ag_{21}(SR)_{18}$ + $Au_5Ag_{20}(SR)_{18}$	5489	[$Au_4Ag_{21}(SR)_{18}$] + [$Au_7Ag_{43}(SR)_{36}$]		
5610	$Au_5Ag_{20}(SR)_{18}$	5656	$Au_5Ag_{20}(SR)_{18}$ + $Au_6Ag_{19}(SR)_{18}$	5521	[$Au_5Ag_{20}(SR)_{18}$] + [$Au_7Ag_{43}(SR)_{36}$]		
5699	$Au_6Ag_{19}(SR)_{18}$	5745	$Au_6Ag_{19}(SR)_{18}$ + $Au_7Ag_{18}(SR)_{18}$	5582	[$Au_5Ag_{20}(SR)_{18}$] + [$Au_9Ag_{41}(SR)_{36}$]		
5788	$Au_7Ag_{18}(SR)_{18}$	5833	$Au_7Ag_{18}(SR)_{18}$ + $Au_8Ag_{17}(SR)1_8$				
5877	$Au_8Ag_{17}(SR)_{18}$	5922	$Au_8Ag_{17}(SR)_{18}$ + $Au_9Ag_{16}(SR)_{18}$				
6055	$Au_{10}Ag_{15}(SR)_{18}$	6011	$Au_9Ag_{16}(SR)_{18}$ + $Au_{10}Ag_{15}(SR)_{18}$				
6144	$Au_{11}Ag_{14}(SR)_{18}$						
6233	$Au_{12}Ag_{13}(SR)_{18}$						
6322	$Au_{13}Ag_{12}(SR)_{18}$						

References

(1) Marty, M. T.; Baldwin, A. J.; Marklund, E. G.; Hochberg, G. K. A.; Benesch, J. L. P.; Robinson, C. V. Bayesian Deconvolution of Mass and Ion Mobility Spectra: From Binary Interactions to Polydisperse Ensembles. *Anal. Chem.* **2015**, *87* (8), 4370–4376. https://doi.org/10.1021/acs.analchem.5b00140.