Supporting information

Core size conversion: Route for exclusive synthesis of Au_{38} or Au_{40} nanomolecules

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Table S1 showing the reproducibility of the core size conversion reactions.
Figure S1: MALDI MS of the samples collected from the size exclusion chromatography of the crude product from one phase THF synthesis.
Figure S2: MALDI mass spectra of the samples collected from the etching of crude product obtained from one phase THF synthesis.
Figure S3: MALDI mass spectra of the samples collected from the etching of a mixture of Au_{67} and $Au_{103\text{-}105}$.
Figure S4: MALDI mass spectra of the samples from $Au_{103\text{-}105}$ to Au_{40} reaction collected under increased laser fluence
Figure S5: MALDI mass spectrum etching reaction of <Au_{67} to Au_{38}.
Figure S6: MALDI mass spectrum etching reaction of Au_{25} to decomposition.

Table S1 showing the reproducibility of the core size conversion reactions performed in our laboratory between May 2010 – Jan 2014

Serial no	Reaction no	Starting material	End product
1	PN1-32	Au_{67} + Au_{104} + lower clusters	Au_{40} + Au_{38}
2	PN1-40a	Au_{67} + Au_{104} + lower clusters	Au_{40} + Au_{38}
3	PN1-40b	Au_{67} + Au_{104} + lower clusters	Au_{40} + Au_{38}
4	PN1-42a	Au_{67} + Au_{104}	Au_{40}
5	PN1-42b	Au_{67} + Au_{104}	Au_{40}
6	PN1-43	Au_{67} + Au_{104} + lower clusters	Au_{40} + Au_{38}
7	PN1-51a	Au_{67} + Au_{104} + lower clusters	Au_{40} + Au_{38}
8	PN1-51b	Au_{67} + Au_{104} + lower clusters	Au_{40} + Au_{38}
9	PN1-140c	Au_{67}	Au_{40}
10	PN1-178	Au_{104}	Au_{40}
11	PN1-140a	Au_{67} + lower clusters	Au_{40} + Au_{38}
12	PN1-154c	Au_{67}	Au_{40}
13	PN1-154b	Au_{67} + lower clusters	Au_{40} + Au_{38}
14	PN1-159b	Au_{67} + lower clusters	Au_{40} + Au_{38}
15	PN1-178	Au_{104}	Au_{40}
16	PN1-178b	Au_{104}	Au_{40}
17	PN2-61	Au_{67} + Au_{104}	Au_{40}
18	PN2-64	Au_{67} + Au_{104}	Au_{40}
19	PN2-64b	Au_{67}	Au_{40}
20	PN2-67b	Lower clusters	Au_{38}
21	PN2-67c	Au_{104}	Au_{40}
22	PN2-71b	Lower clusters	Au_{38}
23	PN2-73b	Lower clusters	Au_{38}

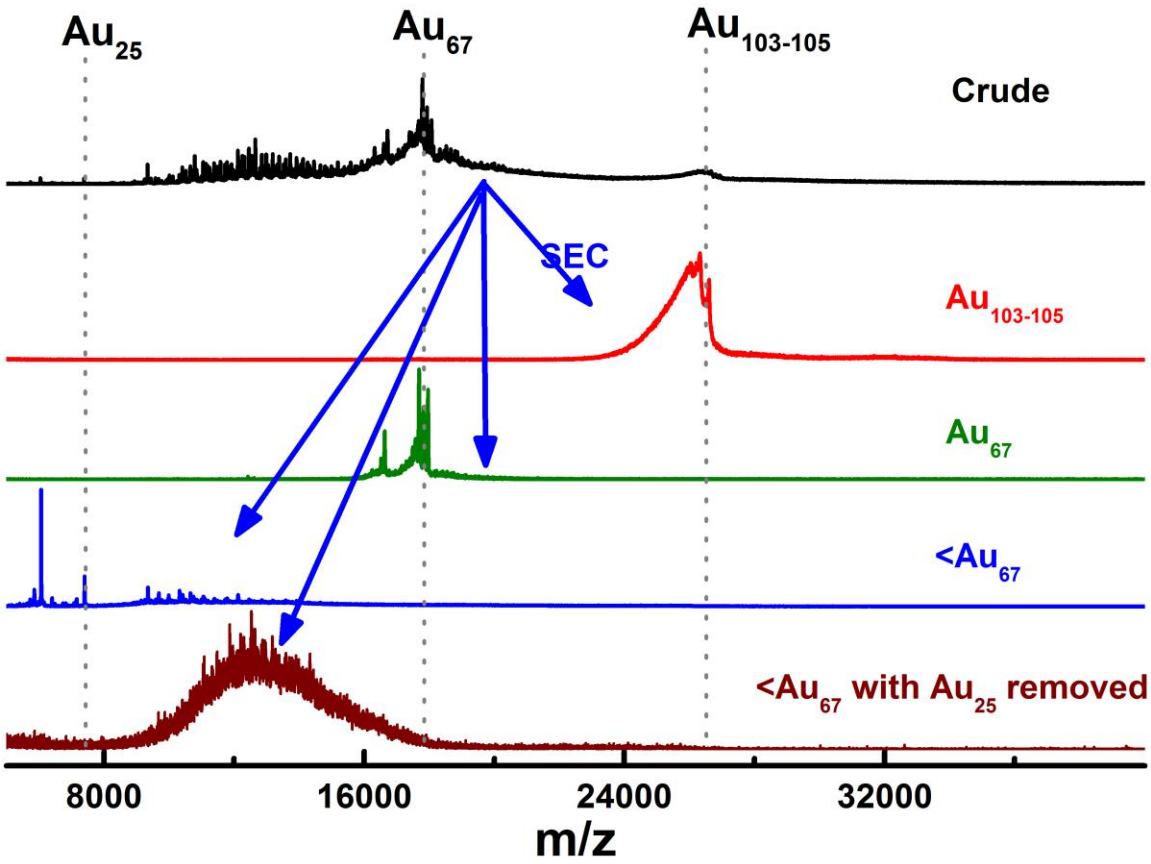

Figure S1: MALDI mass spectra of the fractions (red, olive blue and brown curves) collected from the size exclusion chromatography of the crude product (black curve) obtained from one phase THF synthesis. The $Au_{103\text{-}105}$, Au_{67} and $<Au_{67}$ without Au_{25} obtained here are used for core size conversion reactions in figure 1, figure 2 and figure 3 in the manuscript respectively.

When the crude product obtained from the one phase THF synthesis is etched in the presence of excess thiol at 80 degrees, a mixture of Au_{38} and Au_{40} was obtained.

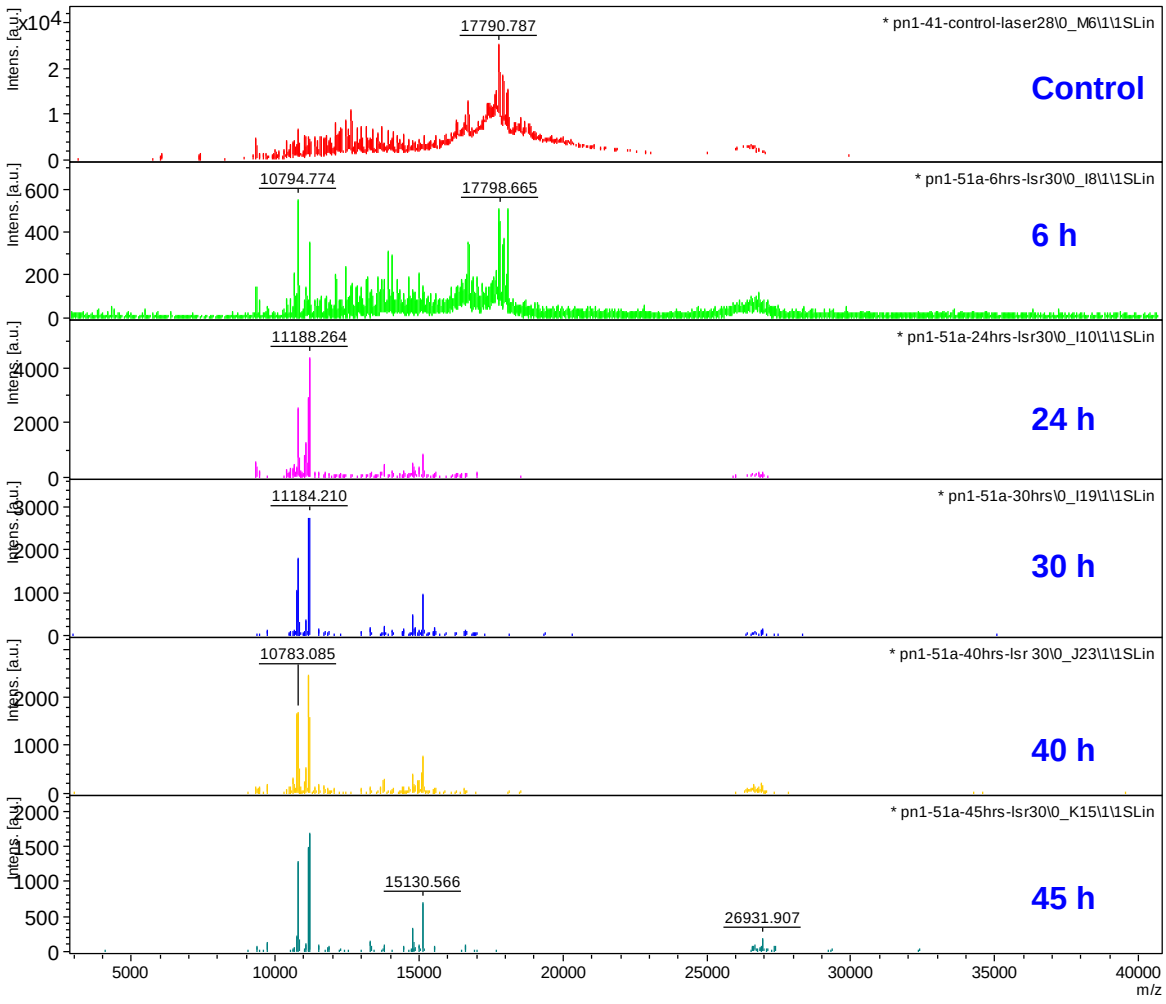

Figure S2: MALDI mass spectra of the samples collected from the etching of crude product obtained from one phase THF synthesis. Note that the crude product contains $Au_{103\text{-}105}$, Au_{67} and lower clusters. Upon etching $Au_{103\text{-}105}$ and Au_{67} core convert to Au_{40} and clusters lower than Au_{67} core convert to Au_{38}, there by yielding a mixture of Au_{38} and Au_{40} in the final product. When the reaction was continued to completion, the 15130 peak disappears in the reaction mixture and Au_{38} and Au_{40} are the only species observed.

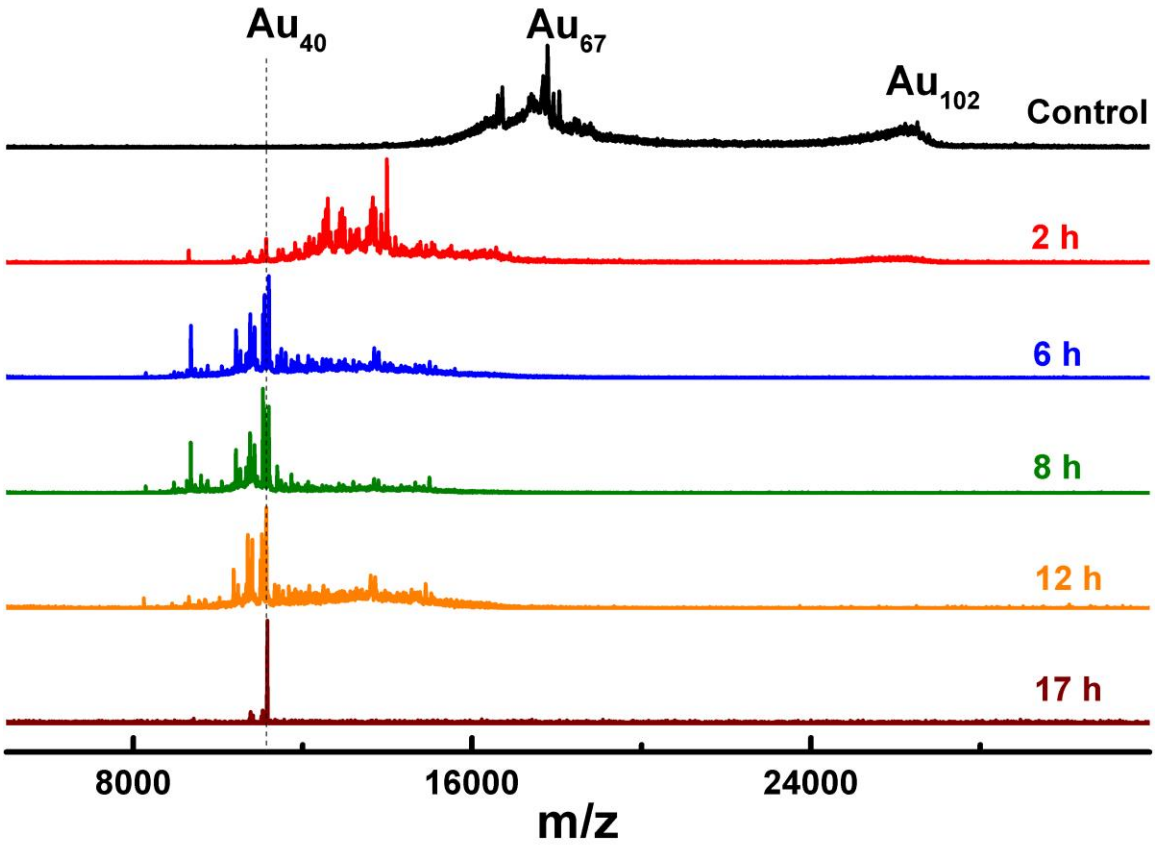

Figure S3: MALDI mass spectra of the samples collected from the etching of a mixture of Au_{67} and $Au_{103\text{-}105}$. Upon etching $Au_{103\text{-}105}$ and Au_{67} core convert to Au_{40}.

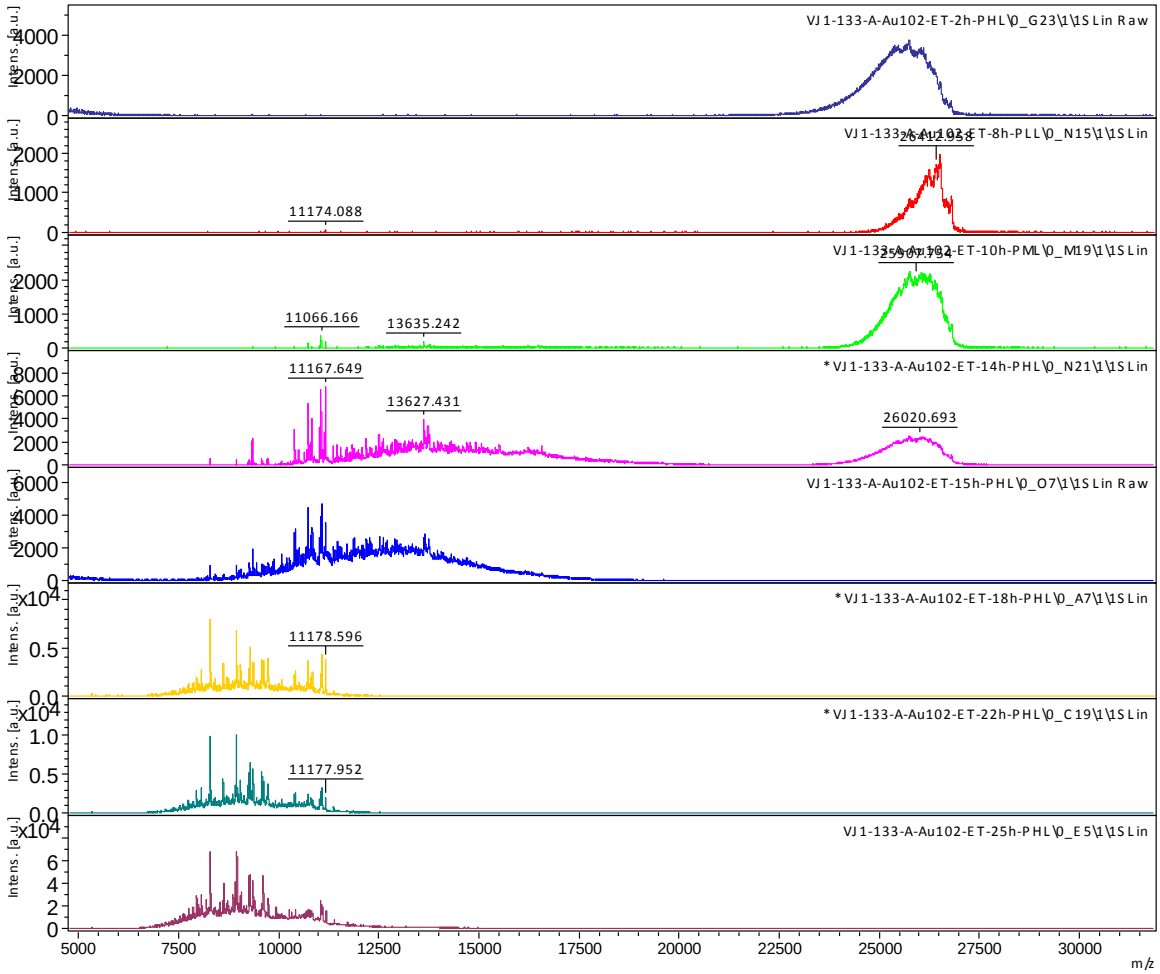

Figure S4: MALDI mass spectra of the samples from $Au_{103\text{-}105}$ to Au_{40} reaction collected under increased laser fluence. The absence of peaks above 11173 Da shows that Au_{40} is the predominant in the end product and was a etching down process.

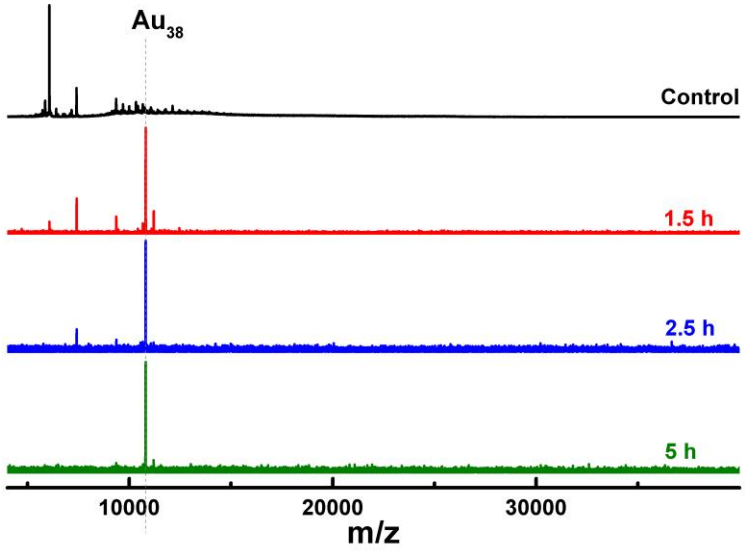

Figure S5: Positive MALDI mass spectra of the samples collected from etching of clusters smaller than Au_{67} in the presence of excess thiol. After 5 h, $Au_{38}(SR)_{24}$ is the predominant product in the reaction mixture. Please note that no $Au_{38}(SR)_{24}$ is present in the initial sample.

Figure S8 shows the MALDI mass spectra of the samples collected from this etching reaction. Note that $Au_{25}(SCH_2CH_2Ph)_{18}$ is present in the starting material. Au_{25} is kinetically stable under certain conditions and is observed in the one phase reaction mixtures even after 3 days.[16] However, Au_{25} has low thermochemical stability in excess thiol and degrades up on etching. Thus, the Au_{25} was not isolated from the starting material used for this etching reaction. In 1.5 h and 2.5 h samples, Au_{38} is abundant with small amount of Au_{25} present in the samples. There is a small peak, with relative intensity lower than Au_{38}, to the right of Au_{38} in 1.5 h and 5 h samples. This peak corresponds to $Au_{40}(SR)_{24}$ and could be originating from minute amounts of larger clusters left in the starting material used. Note that the relative intensity of this peak is very low compared to the Au_{38}.

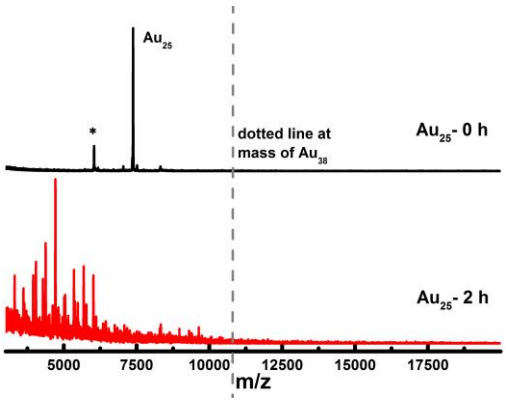

Figure S6: Positive MALDI mass spectra of the sample collected from etching of Au_{25} in the presence of excess thiol. It is a clear indication that the sample is decomposition with time. This decomposition was also evident from the color change of the solution from brown-orange to colorless in 2-3 hrs.