Isolation of Ubiquitous $Au_{40}(SR)_{24}$ Clusters from the 8 kDa Gold Clusters

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Thiolate-protected Au nanoclusters have attracted considerable research interest due to their interesting optical, electronic, and charging properties as well as potential applications in catalysis, biomedicine and nanoelectronics.

When the particle size is less than 2 nm, their structure as well as physical and chemical properties exhibit fundamental differences from those of their larger counterparts.

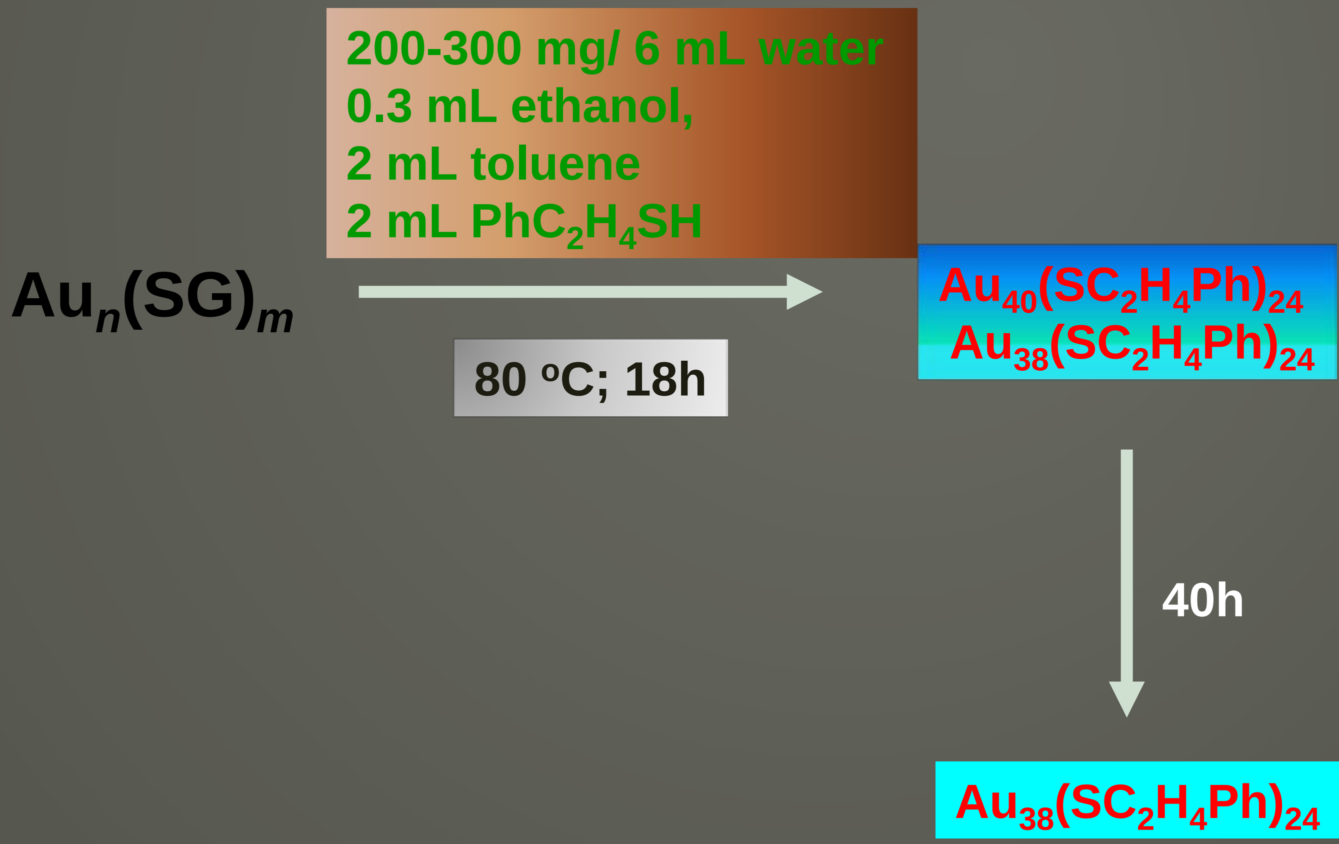
The formula of 5, 8, 14, 22, and 29 kDa have been identified as $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, $Au_{68}(SR)_{34}$, $Au_{102}(SR)_{44}$, and $Au_{144}(SR)_{60}$, respectively with the efforts of multiple research groups.

In addition, some other well-defined clusters have been attained, e.g., $Au_{20}(SR)_{16}$.

Preparation of $Au_n(SG)_m$ mixture ($38 \leq n \leq 102$)

$HAuCl_4 \cdot 3H_2O$ + GSH → (Acetone; 0 °C, 20 min) → yellow cloudy suspension → ($NaBH_4$) → black ppt

Preparation of $Au_{40}(SC_2H_4Ph)_{24}$ and $Au_{38}(SC_2H_4Ph)_{24}$ mixture via thermal thiol etching process



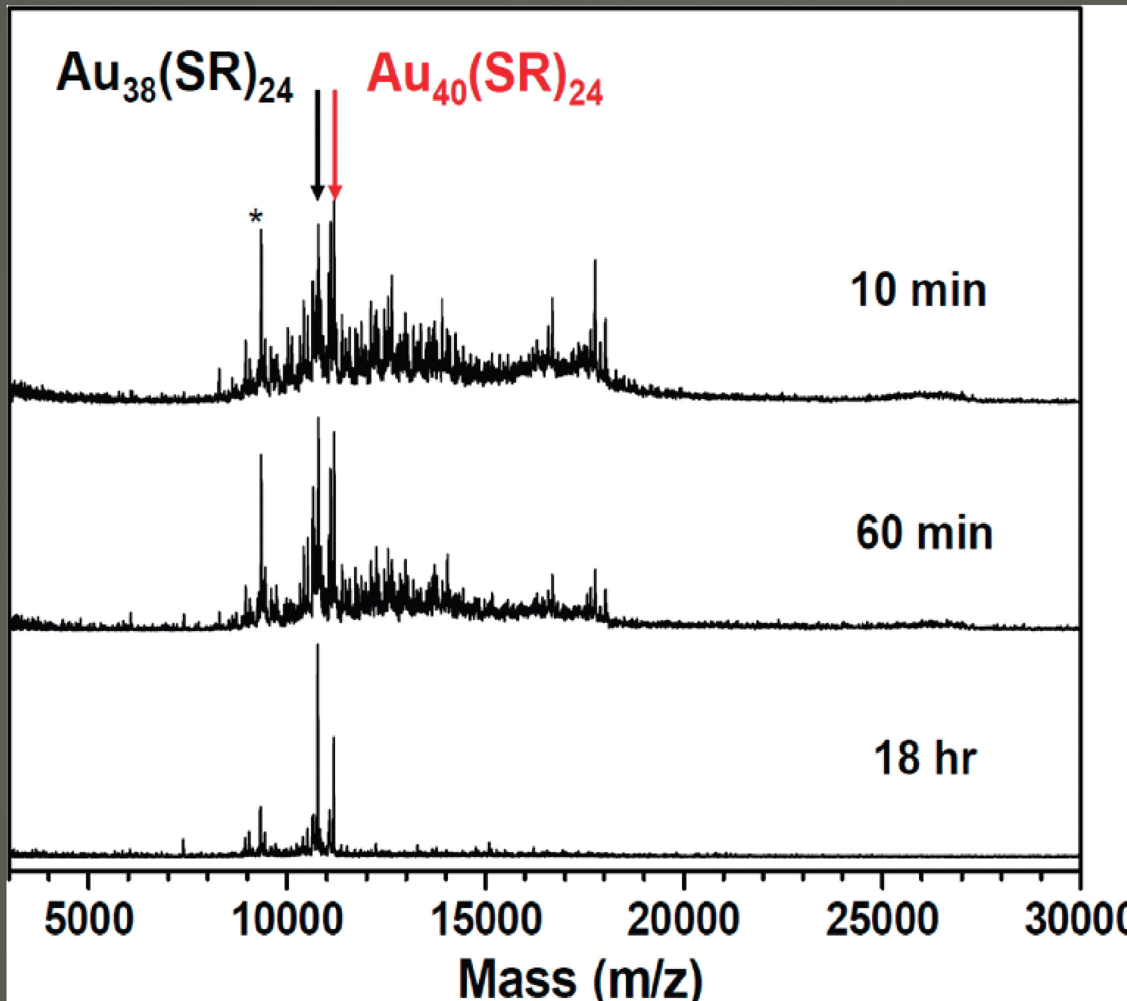
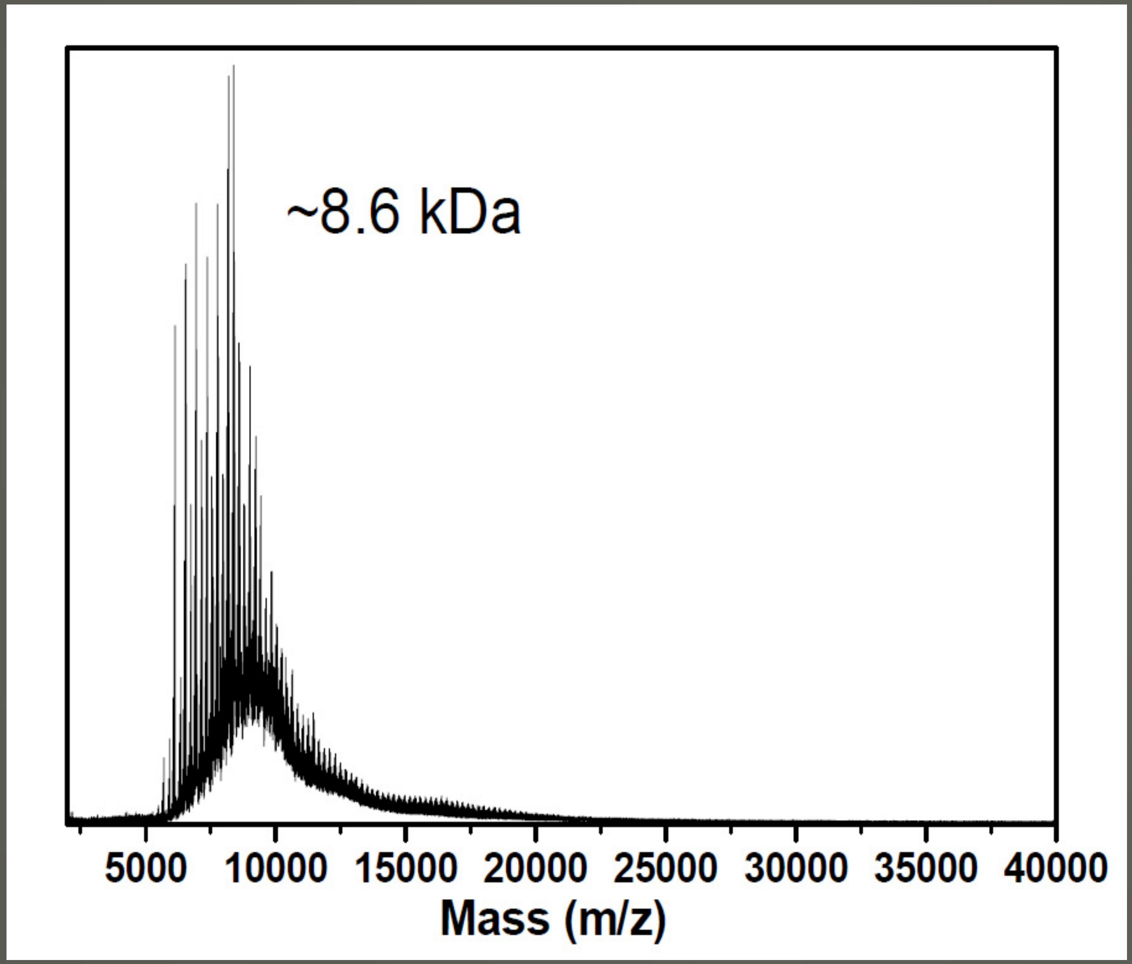


Figure 1. **MALDI mass spectra of $Au_n(SC_2H_4Ph)_m$ clusters after thermal thiol etching for different times.**



Core mass of cluster 1 (~8.6 kDa) determined by MS at high laser intensities

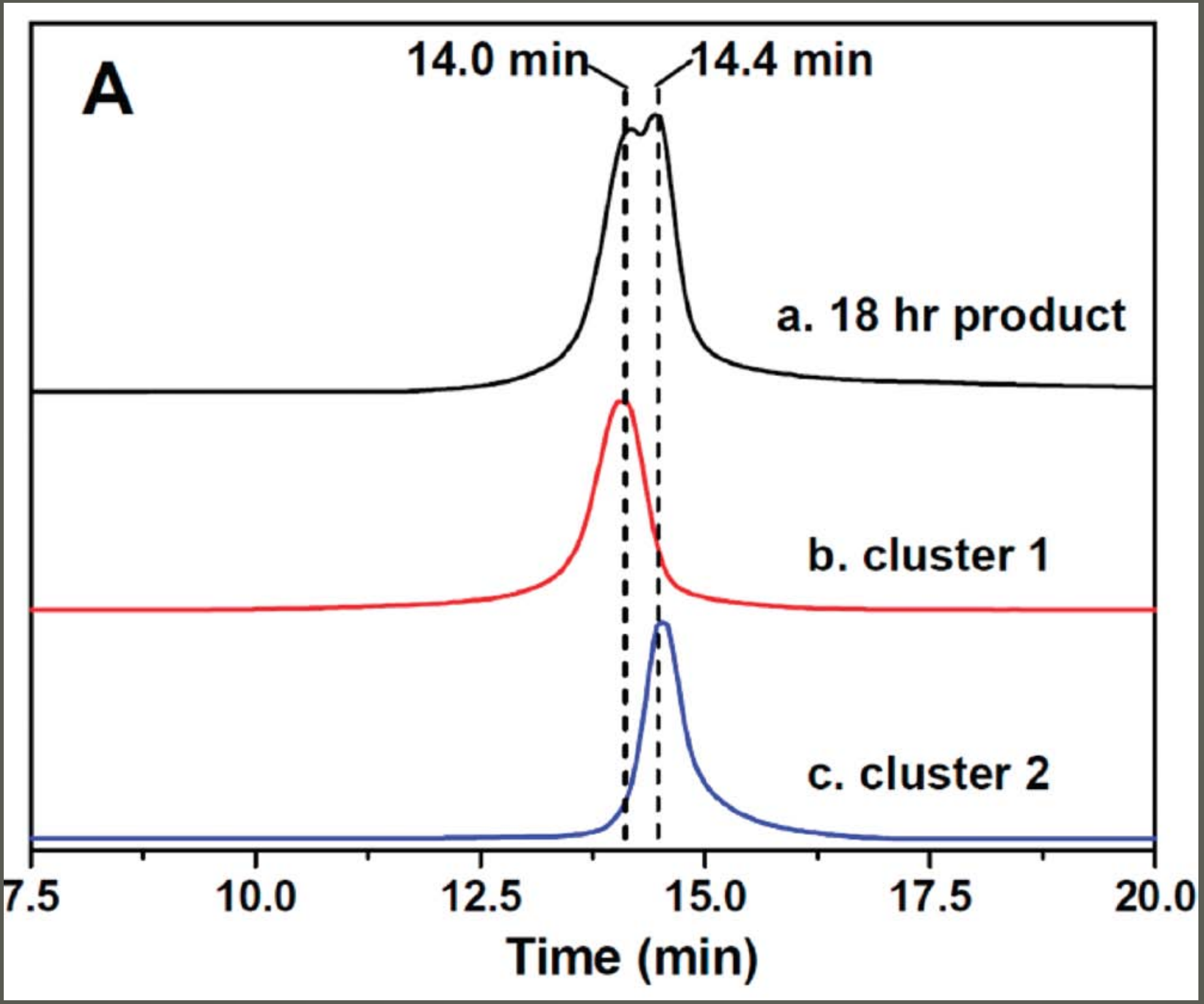
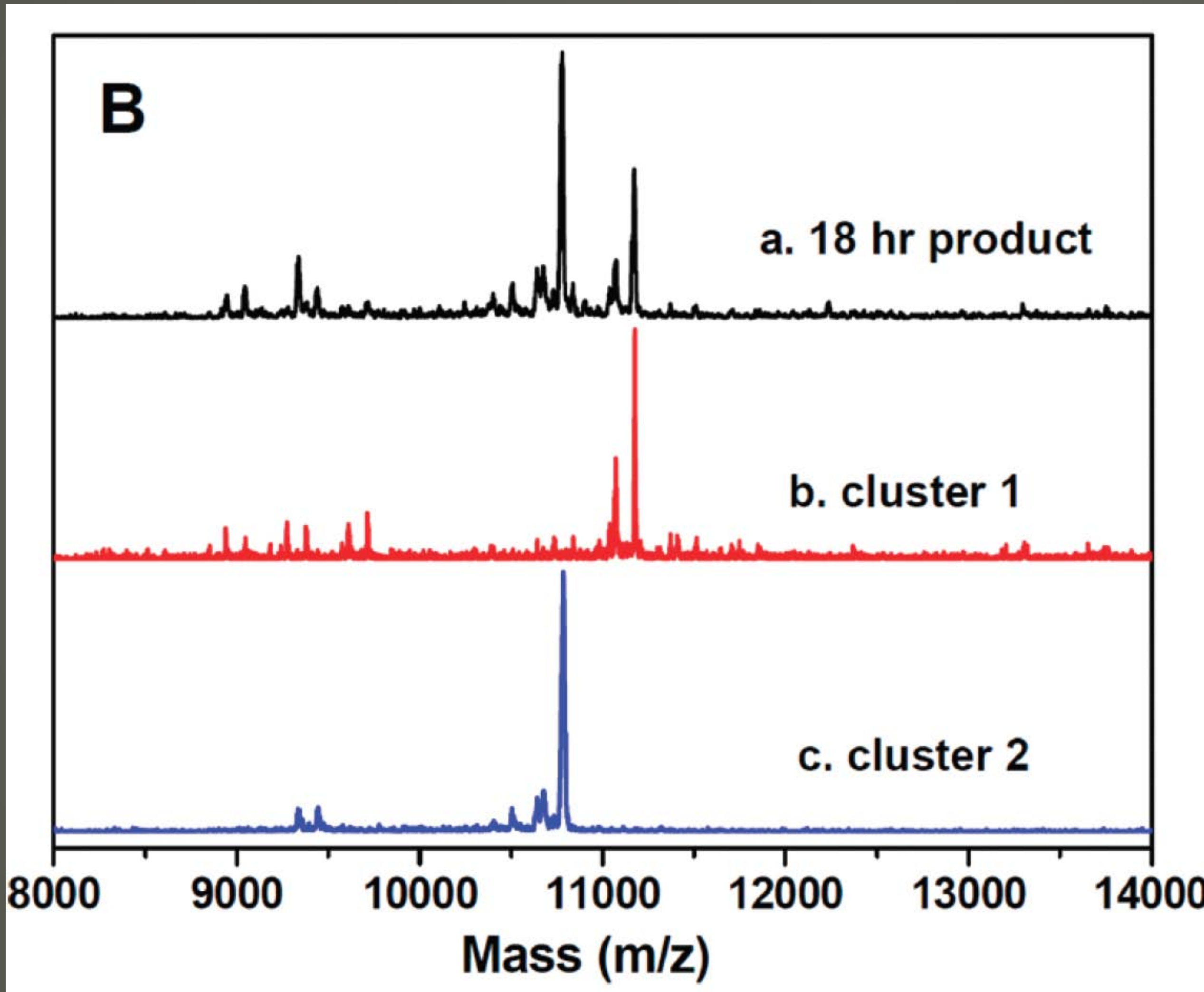


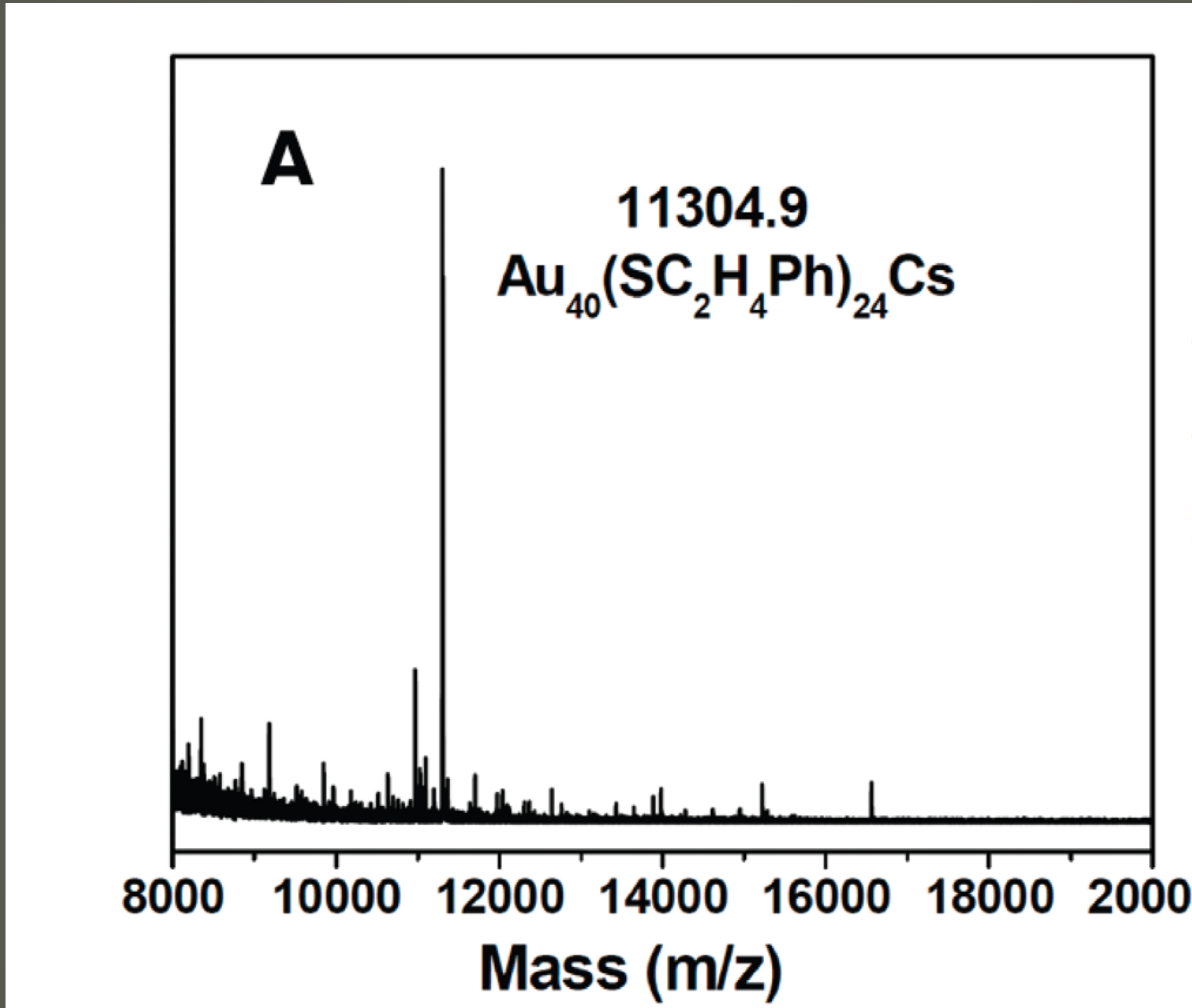
Figure 2. **(A) SEC chromatograms of clusters (monitored by DAD at 750 nm wavelength).**



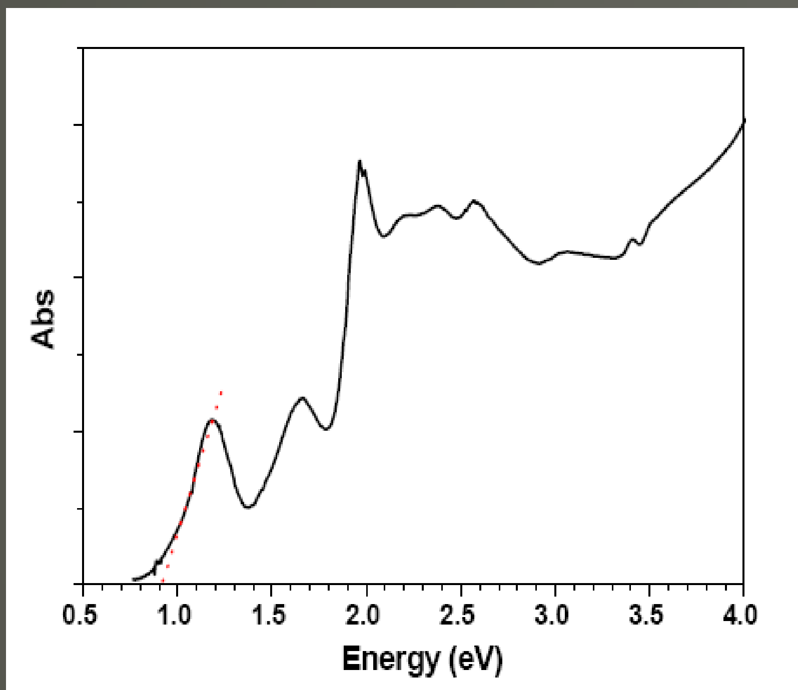
MALDI mass spectra of the crude product and isolated clusters (1 and 2)

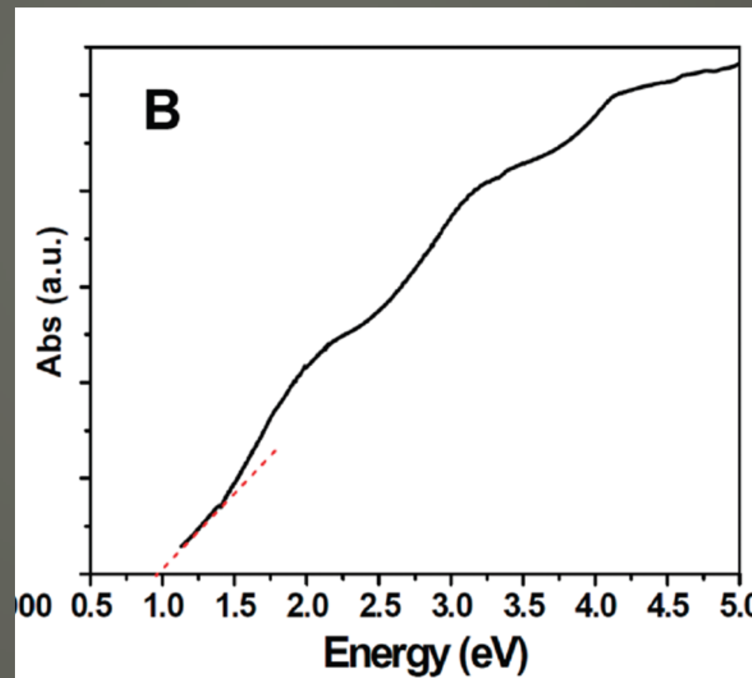
Peaks	Assigned Formula	Theoretical Value	Error
11173.3	$Au_{40}(SC_2H_4Ph)_{24}$	11172.0	1.3
11069.1	$Au_{40}(SC_2H_4Ph)_{23}S$	11066.7	2.4
9711.7	$Au_{34}(SC_2H_4Ph)_{22}$	9715.7	4.0
9609.6	$Au_{34}(SC_2H_4Ph)_{21}S$	9610.6	1.0
9376.3	$Au_{33}(SC_2H_4Ph)_{20}$	9381.6	5.3
9271.9	$Au_{33}(SC_2H_4Ph)_{20}S$	9276.3	4.4
9043.2	$Au_{32}(SC_2H_4Ph)_{20}$	9047.3	4.1

* $Au_{38}(SCH_2CH_2Ph)_{24}$ as an internal reference for mass calibration.

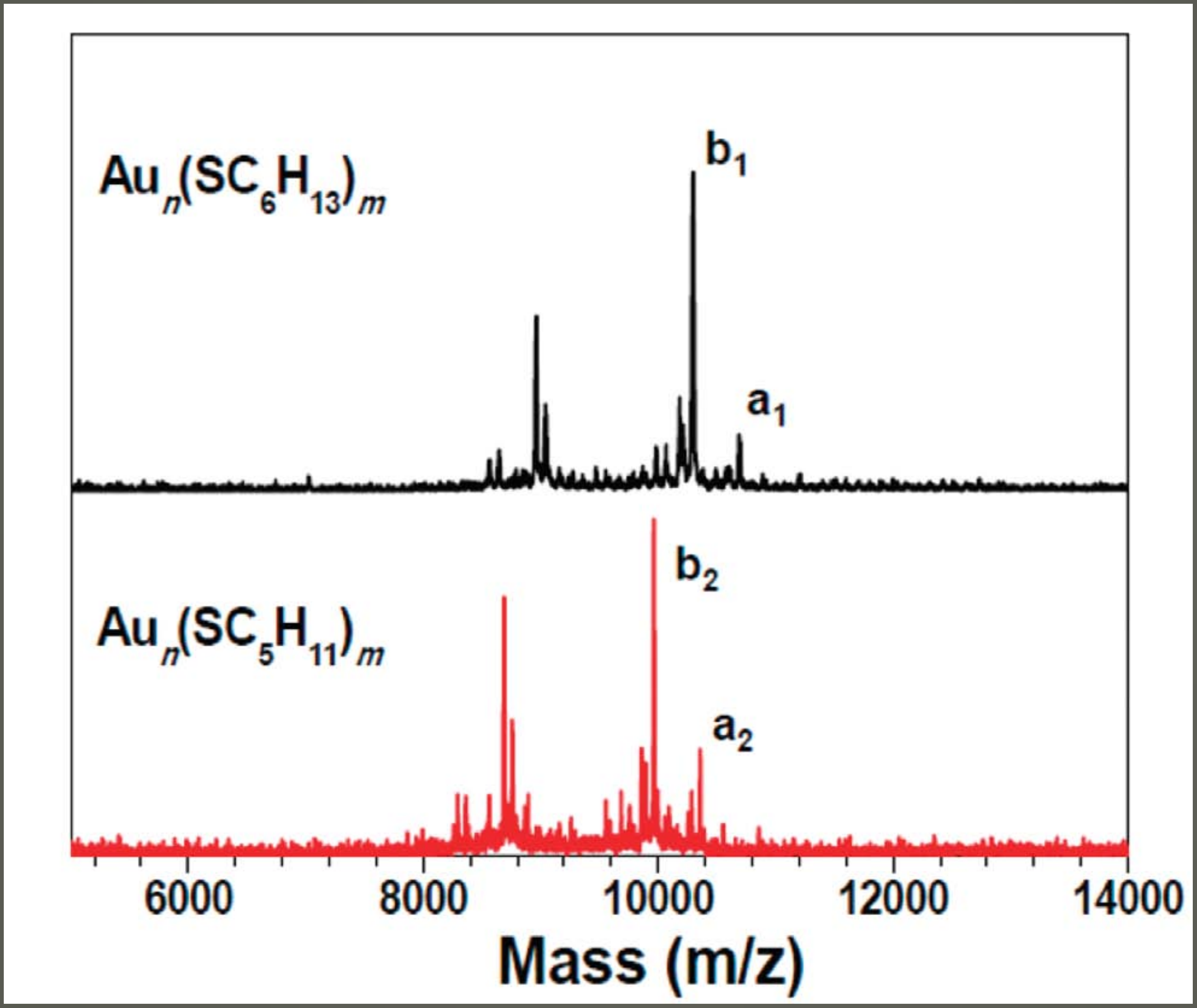


ESI mass spectrum of isolated $Au_{40}(SC_2H_4Ph)_{24}$ clusters.

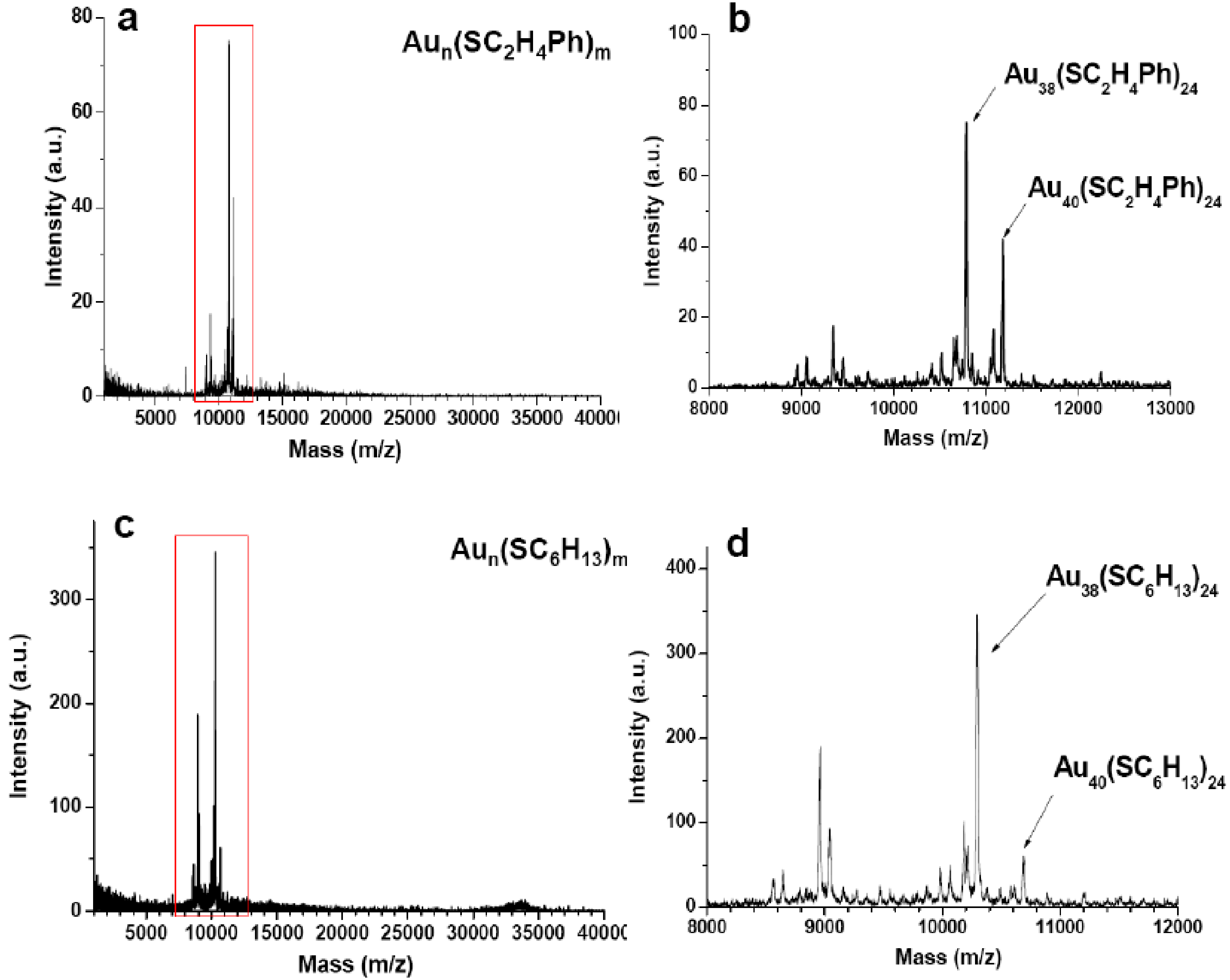




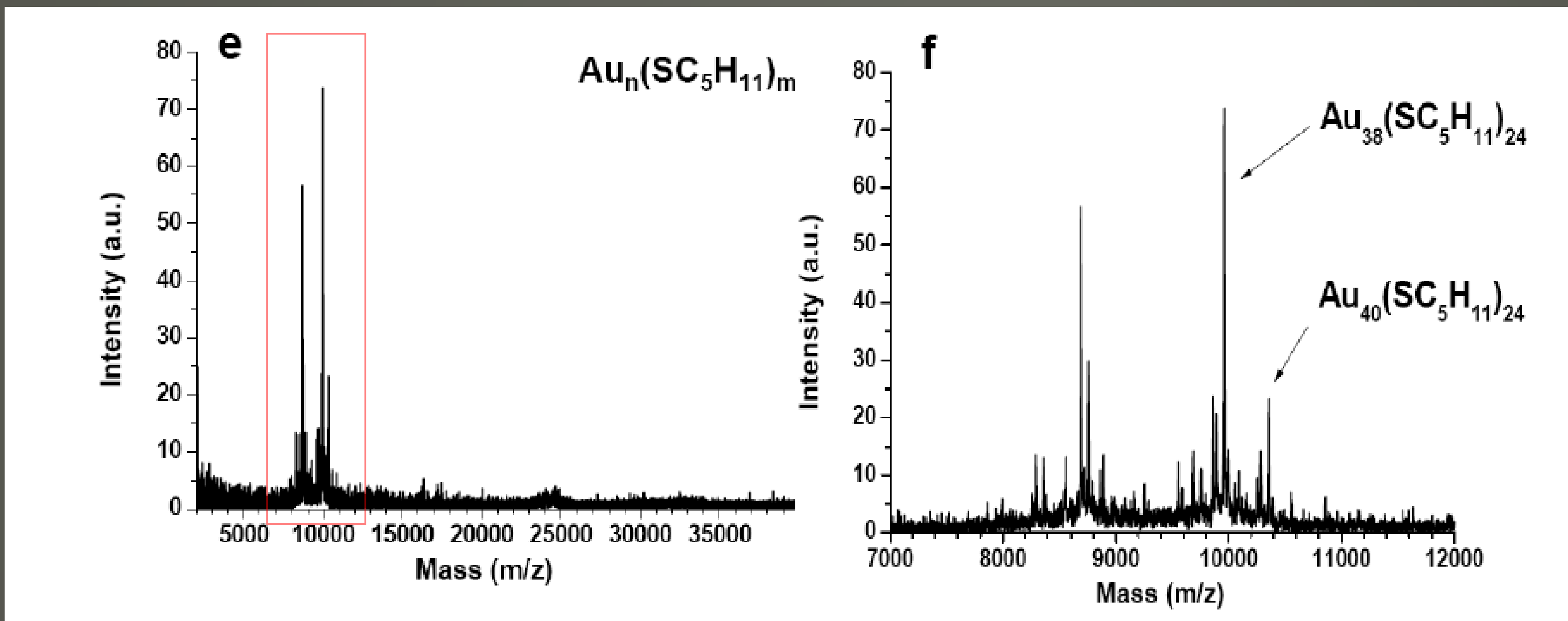
UV-vis spectrum of $Au_{38}(SC_2H_4Ph)_{24}$ clusters (A), $Au_{40}(SC_2H_4Ph)_{24}$ clusters (B)



MALDI mass spectra of $Au_n(SC_6H_{13})_m$ and $Au_n(SC_5H_{11})_m$.
Peak a is from $Au_{40}(SR)_{24}$; peak b is from $Au_{38}(SR)_{24}$.



a
$Au_n(SC_2H_4Ph)_m$
Intensity (a.u.)
Mass (m/z)
b
$Au_{38}(SC_2H_4Ph)_{24}$
$Au_{40}(SC_2H_4Ph)_{24}$
Intensity (a.u.)
Mass (m/z)
c
$Au_n(SC_6H_{13})_m$
Intensity (a.u.)
Mass (m/z)
d
$Au_{38}(SC_6H_{13})_{24}$
$Au_{40}(SC_6H_{13})_{24}$
Intensity (a.u.)
Mass (m/z)



e
$Au_n(SC_5H_{11})_m$
Intensity (a.u.)
Mass (m/z)
f
$Au_{38}(SC_5H_{11})_{24}$
$Au_{40}(SC_5H_{11})_{24}$
Intensity (a.u.)
Mass (m/z)

	Peaks	Assigned Formula	Theoretical Value	Error
Figure a, b	11175.7	$Au_{40}(SC_2H_4Ph)_{24}$	11171.9	3.8
	10780.5	$Au_{38}(SC_2H_4Ph)_{24}$	10778.05	2.4
	9341.9	$Au_{34}(SC_2H_4Ph)_{19}S$	9336.1	5.8
Figure c, d	10691.2	$Au_{40}(SC_6H_{13})_{24}$	10692.2	1.0
	10295.6	$Au_{38}(SC_6H_{13})_{24}$	10298.3	2.7
	8962.4	$Au_{34}(SC_6H_{13})_{19}S$	8956.3	6.1
Figure e, f	10357.6	$Au_{40}(SC_5H_{11})_{24}$	10355.7	1.9
	9962.4	$Au_{38}(SC_5H_{11})_{24}$	9961.6	0.8
	8686.7	$Au_{34}(SC_5H_{11})_{19}S$	8689.8	3.1

The $Au_{40}(SR)_{24}$ formula indicates that the cluster has 16 free electrons (assuming each thiolate consumes one 6s electron of gold).
The electron count is $2e^-$ more than that of $Au_{38}(SR)_{24}$.

From previous reports $Au_{38}(SR)_{24}$ should possess a face-fused biicosahedral Au_{23} core and that the core is further capped by three S-Au-S and six S-Au-S-Au-S staples residing on the Au_{23} waist and two ends, respectively.

Table 1. Possible Structural Models of $Au_{40}(SCH_2CH_2Ph)_{24}$ Clusters

Number of $Au_2(SR)_3$ staples	Number of $Au(SR)_2$ staples	Au core
8	0	Au_{24}
6	3	Au_{25}
4	6	Au_{26}
2	9	Au_{27}
0	12	Au_{28}

Summary:

- Identified a new gold-thiolate cluster and isolated it from the ~8 kDa clusters containing $Au_{38}(SC_2H_4Ph)_{24}$.
- The cluster formula is determined to be $Au_{40}(SC_2H_4Ph)_{24}$ by both MALDI and ESI-MS.
- Unlike $Au_{38}(SC_2H_4Ph)_{24}$ clusters, the UV-vis spectrum of $Au_{40}(SC_2H_4Ph)_{24}$ clusters shows less prominent absorption peaks.
- This cluster constitutes another robust and ubiquitous species in the collection of $Au_n(SR)_m$ *clusters and is useful for future* studies of their new properties and potential applications such as in catalysis.
- The isolation of $Au_{40}(SC_2H_4Ph)_{24}$ indicates that the previous 8 kDa (core mass) Au cluster species should contain two stable clusters (Au_{38} and Au_{40}), though $Au_{38}(SR)_{24}$ is slightly more robust than $Au_{40}(SR)_{24}$.