JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
COMMUNICATION
pubs.acs.org/JACS

$Au_{36}(SPh)_{23}$ Nanomolecules

Praneeth Reddy Nimmala and Amala Dass*

Department of Chemistry and Biochemistry, University of Mississippi, University, Mississippi 38677, United States

S Supporting Information

ABSTRACT: A new core size protected completely by an aromatic thiol, $Au_{36}(SPh)_{23}$, is synthesized and characterized by MALDI-TOF mass spectrometry and UV−visible spectroscopy. The synthesis involving core size changes is studied by MS, and the complete ligand coverage by aromatic thiol group is shown by NMR.

Gold nanomolecules are entities in the nanometer size regime that contain a specific number of gold atoms and passivating organic thiolate ligands with distinct chemical and physical properties. It can be synthesized reproducibly, in large quantities, and characterized precisely by commercially available mass spectrometers, and its size dependent properties studied by spectroscopic methods.[1−3]

Among the various nanomolecules, $Au_{25}(SR)_{18}$ and $Au_{144}(SR)_{60}$ are the most studied experimentally due to their greater stability.[4−9] Other reports on Au_{38}, Au_{68}, and Au_{102} have also been published.[10−12] Theoretical studies have greatly aided in understanding the stability and electronic transitions of these nanomolecules.[13−17]

Au_{38} nanomolecules are unique in their synthetic preparation; an etching step[18] is invariably used as opposed to the more common two phase synthesis.[19,20] First reported by Schaaff, et al.[18] and identified[21] by Tsukuda as $Au_{38}(SR)_{24}$, more recent work by several other groups document its synthesis,[10,22] structure,[23] and electrochemical[24] properties.

Passivating ligands can be varied to obtain nanomolecules of desired solubility based on the end application. They can also impart functionality such as fluorescent, electrochemical, and chiral signature.[25] Ideally, an aromatic group attached directly to the nanoparticle can aid in fast electron transfer and also facilitate in the tuning of the properties of the nanomolecules by inductive effects. Here we report the synthesis of $Au_{36}(SPh)_{23}$. It was synthesized by etching a polydisperse nanocluster mixture in excess thiophenol, and its composition was identified by mass spectrometry and further characterized by optical and NMR spectroscopic data, all pointing to its molecular nature.

A MALDI TOF spectrum of $Au_{36}(SPh)_{23}$ is shown in Figure 1 using a DCTB matrix[26] in positive linear mode on a Bruker Autoflex mass spectrometer. $Au_{32}(SPh)_{19}$ and $Au_{32}(SPh)_{20}$ fragments are seen even at threshold laser intensity. $Au_4(SR)_4$ loss due to fragmentation has been observed before.[27] The MALDI spectrum attests to the monodisperse nature of $Au_{36}(SPh)_{23}$. ESI-MS analysis of the sample was not successful to date possibly due to the neutral charge state.

Nanoparticles in the 10−50 nm size range show a surface Plasmon peak centered around 530 nm, which is size independent.[28] However, gold nanomolecules that are <2 nm show distinct electronic features in the UV−visible region.[29,30] $Au_{36}(SPh)_{23}$ shows a peak at 566 nm and two shoulders at 430 and 370 nm (Figure 2).

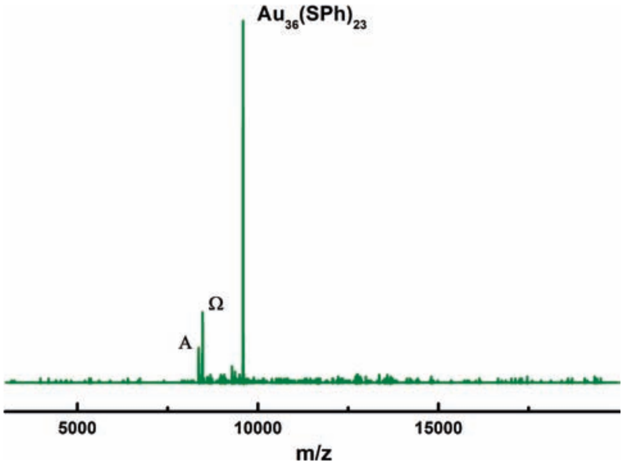

Figure 1. MALDI-TOF mass spectrum of $Au_{36}(SPh)_{23}$ using DCTB matrix in positive linear mode. The fragment peaks denoted by A and Ω are $Au_{32}(SPh)_{19}$ and $Au_{32}(SPh)_{20}$ respectively.

Similar to other Au_{38} synthesis, the preparation of Au_{36} involves two stages. The first stage is the preparation of a mixture that contains Au_{68} and Au_{102} as major species. The second stage is an etching process in large excess of thiophenol. Briefly, in stage 1, 0.1 g (0.25 mmol) of $HAuCl_4 \cdot 3H_20$ was dissolved in 10 mL of THF. While stirring rapidly (500 rpm), 210 μL of (0.5 mmol) of phenylethanethiol ($HSCH_2CH_2Ph$) were added at room temperature. After 1 h, as the solution turned colorless, 0.1 g of $NaBH_4$ dissolved in 2 mL of cold water was added to the reaction instantaneously. The reaction mixture turned black indicating formation of <2 nm Au particles. After 10 min, the reaction was stopped, solvents were removed by rotary evaporation, and the product washed with methanol. In stage 2, a mixture of the purified product in 1.5 mL of THF and 1 mL of thiophenol (HSPh) fitted with a reflux condensor was maintained in an oil bath at 80 °C under vigorous stirring (500 rpm).

Figure 3 shows the MALDI-TOF spectra of samples taken during the etching step that describes the size evolution process leading to the formation of $Au_{36}(SPh)_{23}$ nanomolecules. The purified product after stage 1, the 0 min plot in the figure, contains a mixture of Au_{68} and Au_{102} product with $-SCH_2CH_2Ph$ ligands. Upon etching at 80 °C for 1 h, a major portion of the sample mixture has already converted to a 10 498 Da species.

Received: February 23, 2011
Published: May 31, 2011

dx.doi.org/10.1021/ja201685f | J. Am. Chem. Soc. 2011, 133, 9175–9177

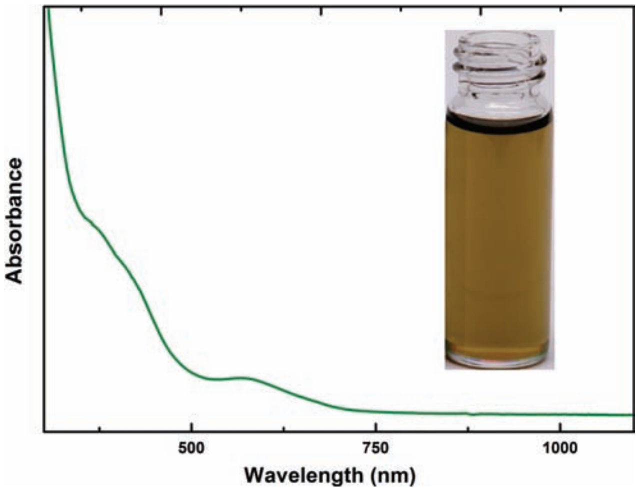

Figure 2. UV−vis spectrum of $Au_{36}(SPh)_{23}$ nanomolecules in toluene. Inset shows a photograph of the toluene solution of the nanomolecule.

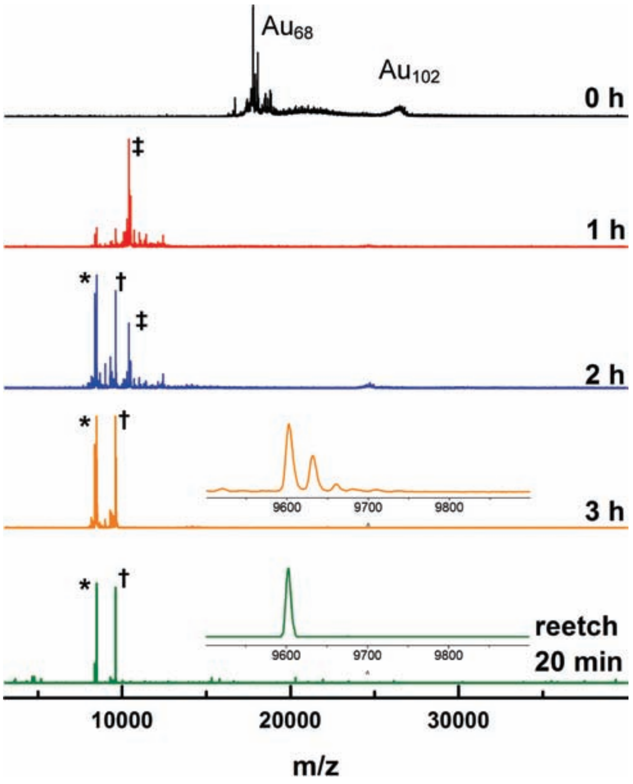

Figure 3. MALDI-TOF spectra of the etching step in excess thiophenol at 80 °C showing the size evolution process involved in the formation of $Au_{36}(SPh)_{23}$ nanomolecules. Inset shows the expanded view of the Au_{36} peak at 9601 Da. Peaks marked by ‡, †, and * indicate $Au_{38}(SR1)_{14}(SR2)_{10}$, $Au_{36}(SR)_{23}$, and $Au_{32}(SR)_{20}$ fragment.

After 2 h, the ~10 400 peak further continues to evolve into a 9601 peak. At the end of 3 h, the sample mainly contains a 9601 peak that corresponds to $Au_{36}(SPh)_{23}$.

Two points are notable in this figure that corresponds to the new core size (Au_{36}) formation and its complete ligand coverage by an aromatic thiol, −SPh. The precursors containing Au_{68} and Au_{102} are completely protected by $-SCH_2CH_2Ph$ ligands. First, the peak at 10 498 Da is $Au_{38}(SCH_2CH_2Ph)_{14}(SPh)_{10}$. So, Au_{38} is an intermediate species with special stability associated with the 14−10 combination of ligand mixture. As the number of aromatic ligands exceeds 10, it appears that the aromaticity imparted to the Au_{38} nanomolecules by the thiophenol ligands reaches a threshold value that leads to change of core size to Au_{36} instead of Au_{38}. The conversion of core size to Au_{38} occurring in ~1 h is relatively fast compared to other reported syntheses. This is due to the higher reactivity of thiophenol ($pK_a = 6.6$)[31] compared to other aliphatic ligands. Second, of the 23 ligands in $Au_{36}(SPh)_{23}$, the final two or three ligands are extremely difficult to exchange. These final two or three ligands can be effectively exchanged without compromising yield, if a second etching is repeated again with fresh thiophenol to drive the reaction to completion (see transition from orange to green plot in Figure 3).

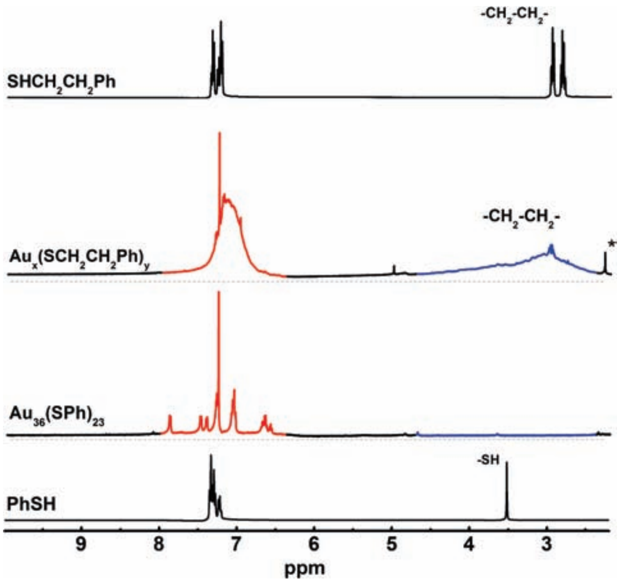

Figure 4. ^1H NMR spectra of $Au_{36}(SPh)_{23}$ nanomolecules, starting material and neat thiols in $CDCl_3$. The red region of the curve in the starting material and product show change of size to smaller clusters. The blue region of the curve shows a complete loss of the original aliphatic protons in the 2.4 to 5 ppm region.

The ^1H NMR spectra in $CDCl_3$ of the purified $Au_{36}(SPh)_{23}$ are shown to confirm the complete coverage by aromatic thiol. The starting material is a mixture of Au_{68} and Au_{102} denoted as $Au_x(SCH_2CH_2Ph)_y$ in Figure 4. The aliphatic, $-CH_2CH_2-$ protons are seen at 2.84 and 2.96 ppm in phenylethanethiol. In the starting material, these are seen as broad peaks between 2.4 and 5 ppm. On etching, the product shows a completely flat baseline in the 2.4−5 ppm region, indicating complete exchange by the all-aromatic thiophenol. Other peaks denoted by an asterisk are due to residual solvents. In the aromatic region, 6−8 ppm, the broad peak in the starting material has become several narrow peaks in the final product. This suggests formation of a smaller core size in the final product in agreement with the MALDI-TOF data. The multiple peaks in the final Au_{36} product attest to its purity and molecular nature.

$Au_{38}(SR)_{24}$ nanomolecules have a Au_{23} core protected by six [−SR−Au−SR−Au−SR−] long staples and three [−SR−Au−SR−] short staples.[16,23] We propose that the structure of $Au_{36}(SR)_{23}$ has Au_{23} core atoms protected by three [−SR−Au−SR−Au−SR−] staples and seven [−SR−Au−SR−] staples. As the core size of the nanomolecules decreases, the number of longer staples increases to account for the spherical nature. The proposed structure for $Au_{36}(SR)_{23}$ does not follow this trend. Efforts to confirm the molecular formula with other aromatic thiols are underway, and single crystal XRD will ultimately reveal the structure. Assuming a neutral charge state, $Au_{36}(SR)_{23}$ has 13 free electrons. The stability of 13 e^{-}s is not predicted by a spherical jellium model and may be attributed to the nonspherical nature of the related class of $\sim Au_{38}$ size clusters.

$Au_{36}(SPh)_{23}$ is the first report of (a) 36 core sized gold nanomolecules and (b) a fully aromatic thiol passivation with a well-defined core and ligands. Aromatic groups provide good electronic coupling with substitutent groups and fast electron transfer characteristics.[31−33] Theoretical studies may explain why an aromatic passivation leads to a stable 36 core instead of 38 and the particular stability of the $Au_{38}(SCH_2CH_2Ph)_{14}(SPh)_{10}$ intermediate.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Synthetic conditions, calibration data, and expanded MS and NMR figures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

amal@olemiss.edu

■ ACKNOWLEDGMENT

We gratefully acknowledge support from NSF 0903787, University of Mississippi Startup Fund, and CLA summer research grant. We thank Charles Hussey, Glenn Hopkins, and College of Liberal Arts for Bruker Autoflex MALDI TOF instrumentation support and T. Keith Hollis for helpful suggestions.

■ REFERENCES

(1) Whetten, R. L.; Khoury, J. T.; Alvarez, M. M.; Murthy, S.; Vezmar, I.; Wang, Z. L.; Stephens, P. W.; Cleveland, C. L.; Luedtke, W. D.; Landman, U. *Adv. Mater.* **1996**, *8*, 428–433.

(2) Templeton, A. C.; Wuelfing, M. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27–36.

(3) Jin, R. *Nanoscale* **2010**, *2*, 343–362.

(4) Heaven, M. W.; Dass, A.; White, P. S.; Holt, K. M.; Murray, R. W. *J. Am. Chem. Soc.* **2008**, *130*, 3754–3755.

(5) Shichibu, Y.; Negishi, Y.; Tsunoyama, H.; Kanehara, M.; Teranishi, T.; Tsukuda, T. *Small* **2007**, *3*, 835–839.

(6) Schaaff, T. G.; Shafigullin, M. N.; Khoury, J. T.; Vezmar, I.; Whetten, R. L. *J. Phys. Chem. B* **2001**, *105*, 8785–8796.

(7) Qian, H.; Jin, R. *Nano Lett.* **2009**, *9*, 4083–4087.

(8) Fields-Zinna, C. A.; Sardar, R.; Beasley, C. A.; Murray, R. W. *J. Am. Chem. Soc.* **2009**, *131*, 16266–16271.

(9) Lopez-Acevedo, O.; Akola, J.; Whetten, R. L.; Gronbeck, H.; Hakkinen, H. *J. Phys. Chem. C* **2009**, *113*, 5035–5038.

(10) Toikkanen, O.; Ruiz, V.; Ronholm, G.; Kalkkinen, N.; Liljeroth, P.; Quinn, B. M. *J. Am. Chem. Soc.* **2008**, *130*, 11049–11055.

(11) Dass, A. *J. Am. Chem. Soc.* **2009**, *131*, 11666–11667.

(12) Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Bushnell, D. A.; Kornberg, R. D. *Science* **2007**, *318*, 430–433.

(13) Walter, M.; Akola, J.; Lopez-Acevedo, O.; Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Whetten, R. L.; Gronbeck, H.; Hakkinen, H. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 9157–9162.

(14) Pei, Y.; Gao, Y.; Zeng, X. C. *J. Am. Chem. Soc.* **2008**, *130*, 7830–7832.

(15) Akola, J.; Walter, M.; Whetten, R. L.; Hakkinen, H.; Gronbeck, H. *J. Am. Chem. Soc.* **2008**, *130*, 3756–3757.

(16) Lopez-Acevedo, O.; Tsunoyama, H.; Tsukuda, T.; Håkkinen, H.; Aikens, C. M. *J. Am. Chem. Soc.* **2010**, *132*, 8210–8218.

(17) Zhu, M.; Aikens, C. M.; Hollander, F. J.; Schatz, G. C.; Jin, R. *J. Am. Chem. Soc.* **2008**, *130*, 5883–5885.

(18) Schaaff, T. G.; Whetten, R. L. *J. Phys. Chem. B* **1999**, *103*, 9394–9396.

(19) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801–802.

(20) Hostetler, M. J.; Wingate, J. E.; Zhong, C. J.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; Green, S. J.; Stokes, J. J.; Wignall, G. D.; Glish, G. L.; Porter, M. D.; Evans, N. D.; Murray, R. W. *Langmuir* **1998**, *14*, 17–30.

(21) Chaki, N. K.; Negishi, Y.; Tsunoyama, H.; Shichibu, Y.; Tsukuda, T. *J. Am. Chem. Soc.* **2008**, *130*, 8608–8610.

(22) Qian, H.; Zhu, Y.; Jin, R. *ACS Nano* **2009**, *3*, 3795–3803.

(23) Qian, H.; Eckenhoff, W. T.; Zhu, Y.; Pintauer, T.; Jin, R. *J. Am. Chem. Soc.* **2010**, *132*, 8280–8281.

(24) Toikkanen, O.; Carlsson, S.; Dass, A.; Rönholm, G.; Kalkkinen, N.; Quinn, B. M. *J. Phys. Chem. Lett.* **2010**, 32–37.

(25) Templeton, A. C.; Hostetler, M. J.; Warmoth, E. K.; Chen, S. W.; Hartshorn, C. M.; Krishnamurthy, V. M.; Forbes, M. D. E.; Murray, R. W. *J. Am. Chem. Soc.* **1998**, *120*, 4845–4849.

(26) Dass, A.; Stevenson, A.; Dubay, G. R.; Tracy, J. B.; Murray, R. W. *J. Am. Chem. Soc.* **2008**, *130*, 5940–5946.

(27) Dharmaratne, A. C.; Krick, T.; Dass, A. *J. Am. Chem. Soc.* **2009**, *131*, 13604–13605.

(28) Link, S.; El-Sayed, M. A. *J. Phys. Chem. B* **1999**, *103*, 4212–4217.

(29) Alvarez, M. M.; Khoury, J. T.; Schaaff, T. G.; Shafigullin, M. N.; Vezmar, I.; Whetten, R. L. *J. Phys. Chem. B* **1997**, *101*, 3706–3712.

(30) Wyrwas, R. B.; Alvarez, M. M.; Khoury, J. T.; Price, R. C.; Schaaff, T. G.; Whetten, R. L. *Eur. Phys. J. D* **2007**, *43*, 91–95.

(31) Price, R. C.; Whetten, R. L. *J. Am. Chem. Soc.* **2005**, *127*, 13750–13751.

(32) Chen, S. W.; Murray, R. W. *Langmuir* **1999**, *15*, 682–689.

(33) Guo, R.; Murray, R. W. *J. Am. Chem. Soc.* **2005**, *127*, 12140–12143.