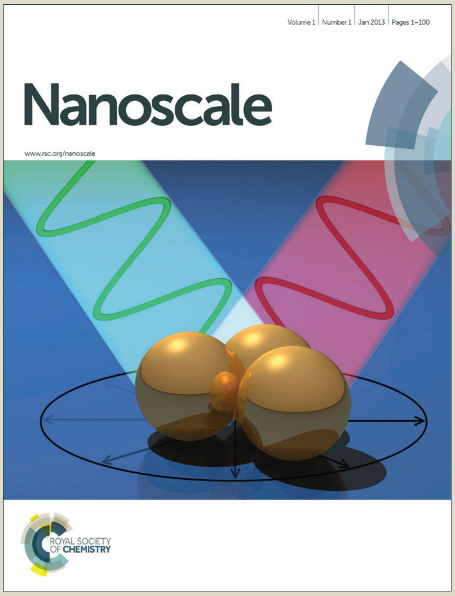
Nanoscale

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/nanoscale

Nanoscale

COMMUNICATION

Synthesis of fluorescent phenylethanethiolated gold nanoclusters via pseudo-AGR method†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Chuanhao Yao,[‡,a] Shubo Tian,[‡,a] Lingwen Liao,[a] Xinfeng Liu,[b] Nan Xia,[a] Nan Yan,[a] Zibao Gan,[a] and Zhikun Wu*[,a]

It's well known that the fluorescence of metal nanoclusters is strongly dependent of the protecting ligand and there is rare report of phenylethanethiolated metal nanoclusters with distinct fluorescence. Herein, a fluorescent phenylethanethiolated gold nanocluster is synthesized using an unexpected pseudo-AGR method (AGR: anti-galvanic reduction). The cluster is precisely determined to be $Au_{24}(SC_2H_4Ph)_{20}$ by isotope-resolved mass spectrum in tandem with thermogravimetric analysis (TGA); the fluorescence comparison between $Au_{24}(SC_2H_4Ph)_{20}$, $Au_{25}(SC_2H_4Ph)_{18}$, $Au_{38}(SC_2H_4Ph)_{24}$ and $Au_{144}(SC_2H_4Ph)_{60}$ is also presented. The finding of fluorescent phenylethanethiolated gold nanocluster in this work has important implication for future study on the fluorescence of metal nanoclusters.

The intrinsic fluorescence of ultrasmall nanoparticles (so-called nanoclusters, opposite to their big counterparts-nanocrystals) has attracted extensive interest not only for fundamental scientific research but also for practical application in a variety of fields such as sensing and biomedicine.[1-12] It is demonstrated that the fluorescence of metal nanoclusters is dependent of the electrical nature of metal core as well as the type of surface ligands.[13-19] Especially for the latter, a number of works from different groups have validated it, and most of the known fluorescent metal nanoclusters contain some electron-rich atom or groups such as N, P and COOH.[14, 20-25] To the best of our knowledge, there are rare reports of fluorescent metal nanoparticles protected by some simple lipophilic ligands which don't containthe above mentioned electron-rich atoms or groups (for instance, phenylethanethiolate). However, basing on the fact that the fluorescence of metal nanoclusters is intrinsic (i.e., not from the ligands), we deem that the phenylethanethiolated metal nanocluster can emit extensive fluorescence after its structure is subtly tuned. To testify the possibility, novel synthesis methods should be developed to synthesize some unique stuctures that are otherwise difficult to obtain on basis of the current, popular methods (mainly Brust-Schiffrin[26-29] and ligand-exchange methods[30-35]). The recently revealed anti-galvanic reduction[36](AGR), initially employed for the synthesis of bimetal nanoclusters (e.g., $Au_{25}Ag_2$),[15] is successfully employed to synthesize mono-metal nanoparticles-$Au_{44}(SC_2H_4Ph)_{32}$ very recently.[37] Inspired by this, we reacted anion $Au_{25}(SC_2H_4Ph)_{18}$ (abbreviated as Au_{25}^-) with Au-SC_2H_4Ph complex, and interestingly, we obtained a fluorescent phenylethanethiolated gold nanoclusters, which is determined to be $Au_{24}(SC_2H_4Ph)_{20}$ (abbreviated as Au_{24}) by electrospray ionization mass spectrometry (ESI-MS), together with thermogravimetric analysis (TGA). Due to the method shows somewhat resemblance to the so-called AGR, it is named pseudo-AGR method. Below we will present more details and discussion.

Recently we reported that AGR is ion-precursor dependent,[38] thus we tried two ion-precursors in the reaction with Au_{25}^-: one is the simple Au salt -$HAuCl_4{\cdot}4H_2O$, and the other is Au-SC_2H_4Ph complex. The synthesis is rather facile and mild. Briefly, excessive $AuCl_4^-$ ions or Au-SC_2H_4Ph complex is dissolved in CH_3CN and then added into a toluene solution of Au_{25}^-. The reaction proceeds for ~ 24 h at room temperature, then is terminated by the addition of a large amount of petroleum ether. The precipitates are collected by centrifugation and washed with CH_3OH for three times. In the case of reaction with $AuCl_4^-$ ion, the color of solution rapidly turns from orange to gray and then to yellow after the addition of $HAuCl_4{\cdot}4H_2O$, precipitates grow more and more with the change of solution color, and the collected solid by centrifuging cannot dissolve in any common solvents such as THF, dichloromethane and DMSO, indicating that formation of very large particles. Transmission electron microscope (TEM) monitors the particle growth process, see Fig. S1 in electronic supplementary information (ESI). While in the case of reaction with Au-SC_2H_4Ph complex, most of the resultant precipitate can dissolve in dichloromethane and subject subsequent separation and purification by thin-layer chromatography (TLC). However, small portion of larger particles (>2 nm) are still observed in the intermediate product (12h), see Fig.

---

[a] *Key Laboratory of Materials Physics, Anhui Key Laboratory of Nanomaterials and Nanostructures, Institute of Solid State Physics, Chinese Academy of Sciences,Hefei, Anhui 230031, China.*
[b] *National Center for Nanoscience and Technology, Chinese Academy of Sciences, Beijing, 100190, China*

†Electronic Supplementary Information (ESI) available: Experimental details, TEM monitoring of the reaction process, digital photos of Au_{24} and Au_{25} under visible and UV light, MALDI-MS spectra of Au_{25}, intermediate product, and Au_{24}, Fluorescence decay profiles of Au_{24}, Au_{25}, Au_{38} and Au_{144} and Photobleaching curve of $Au_{24}(SC_2H_4Ph)_{20}$.

‡ C.Y. and S.T. contributed equally to this work.

S2, indicating somewhat similarity between the two reaction mechanisms. The products discrepancy between the two cases is ascribed to different oxidbillity of the two gold precursors. $HAuCl_4 \cdot 4H_2O$ is far more oxidative than $Au\text{-}SC_2H_4Ph$ complex and it can cause the aggregation of Au_{25}; while the latter is a relatively weak oxidant and induce the formation of a different nanocluster indicated by TLC (Fig. 1a and S3) and some larger nanoparticles (see Fig. S2b). In more details, the transformation could be driven by the oxidation of $HAuCl_4 \cdot 4H_2O$ or $Au\text{-}SC_2H_4Ph$ complex, which destabilizes the core-shelled Au_{25} structure and induced the recombination of Au_{25} to a new nanocluster or larger nanoparticles. Large particles are favorably formed under strong oxidation ($HAuCl_4 \cdot 4H_2O$), while the new nanoclusters are favorably formed under relative weak oxidation ($Au\text{-}SC_2H_4Ph$ complex). In brief, the transformation could be an oxidation-recombination process, which is also supported by the massspectrometry monitoring (see Fig S4-5). Specifically, the observation of RS-SR (SR: SCH_2CH_2Ph, Fig. S4b) indicates the oxidation and protecting-ligand loss of Au_{25}, which could destabilize Au_{25} and lead to the subsequent recombination of Au_{25} nanoparticles.

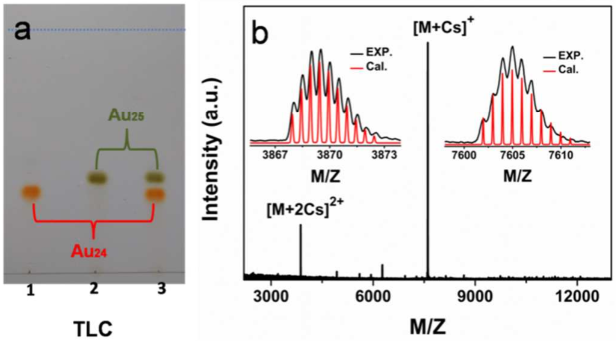


Fig.1 Thin-layer chromatography (TLC) of the as-prepared nanoclusters and Au_{25} (a) and ESI mass spectrum of $Au_{24}(SC_2H_4Ph)_{20}$ (b). (1): The as-prepared nanocluster; (2): Au_{25}; (3): The mixture of Au_{25} and the as-prepared nanocluster. Insets (b) are experimental and calculated isotope patterns of $Au_{24}(SC_2H_4Ph)_{20}Cs^+$ and $Au_{24}(SC_2H_4Ph)_{20}Cs_2^{2+}$, respectively (acquired in the positive ionization mode).

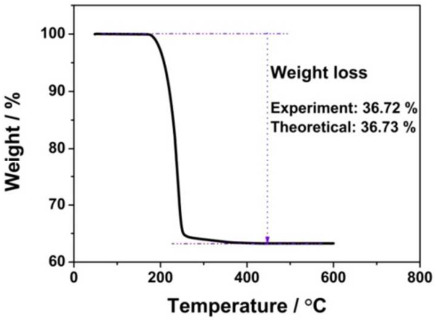


Fig. 2.TGA of $Au_{24}(SC_2H_4Ph)_{20}$

To determine the precise composition of the as-prepared nanocluster, ESI-MS analysis was performed. To impart charges, cesium acetate (CsOAc) was added to the nanocluster solution to form Cs^+ adducts. The ESI-MS spectrum (acquired in positive ionization mode, Fig.1b) shows two intense peaks at m/z 7605.0 and 3869.5 which are readily assigned to $[Au_{24}(SC_2H_4Ph)_{20}Cs]^+$ (calcd. m/z: 7604.96; deviation: 0.04) and $[Au_{24}(SC_2H_4Ph)_{20}Cs_2]^{2+}$ (calcd. m/z: 3869.44; deviation: 0.06), respectively. The well matched experimental and calculated isotope patterns (Fig.1b, inset) confirms the assignment. Thus, the as-prepared nanocluster should have a formular composition of $Au_{24}(SC_2H_4Ph)_{20}$ (abbreviated as Au_{24}) after deducting the adducted Cs^+ ion, and it is neutral since the charge number equals to that of adducted Cs^+ ions. Thermogravimetric analysis (TGA) further confirms the composition. A weight loss of 36.72 % is in perfect agreement with the theoretical values of $Au_{24}(SC_2H_4Ph)_{20}$ (36.73 %), see Fig. 2. Of note, the composition is also similar to some previous reports.[39, 40]

Being ultrasmall, metal nanoclusters exhibit intriguing physicochemical properties highly sensitive to their compositions and structures, and only one metal atom or one thiolate ligand difference in the formular compositions may lead to dramatic difference in their physicochemical properties.[13] The fluorescence of metal nanoclusters has long been an intriguing topic that has drawn considerable research interest in the past two decades.[7, 8, 16, 21, 25] Previous studies revealed that the surface ligands (-SR) played a major role in enhancing the fluorescence of gold nanoparticles.[14] To our knowledge, phenylethanethiolated gold nanoclusters with distinct fluorescent is rarely reported so far. Surprisingly, it is found the as-prepared phenylethanethiolated Au_{24} in this work exhibits bright fluorescence under UV/vis irradiation, in strong contrast to the other several well-defined phenylethanethiolated nanoclusters (including neutral $Au_{25}(SC_2H_4Ph)_{18}$, $Au_{38}(SC_2H_4Ph)_{24}$ and $Au_{144}(SC_2H_4Ph)_{60}$, abbreviated as Au_{25}, Au_{38}, and Au_{144}, respectively) (Fig. 3). For convenience of comparison, their emission spectra were also summarized in Fig. 3, which clearly demonstrates that Au_{24} shows remarkably stronger fluorescence compared with the other several nanoclusters with same protecting ligand (The fluorescence quantum yield of Au_{24} is about 40 times higher than that of Au_{25}, see Fig. 3). To explain this, size effect and ligand effect can be excluded since that their fluorescence intensity are not proportional to the nanoclusters' sizes and they possess the completely same ligand. Previous report indicates that high content of thiolates could be a beneficial factor for the triggering of fluorescence,[13] however, herein we found that the fluorescence intensity of Au_{38} is higher than that of Au_{25} although the thiolate content of Au_{38} is lower than that of Au_{25}. The highest occupied molecular orbital (HOMO)—lowest unoccupied molecular orbital (LUMO) electrical structure could be a consideration: It is found that the gap between the first oxidation and the first reduction potential (which correlates with the HOMO-LUMO gap) enlarges with the decrease of size, and Au_{24} exhibits the largest gap (2.35 V) among the aforementioned nanoclusters (Fig. 4). Another consideration is the metal core structure since the phenylethanethiolate ligand itself is not fluorescent. Unfortunately, further investigation is hindered by the unsuccessful unravelling of the single crystal structures of Au_{24} and Au_{144}. Although three various 24-atom gold core structures were recently revealed,[39-41] it is difficult to assign the structure of Au_{24} to any of them at the current stage since their fluorescence have not been reported by now. Au_{24} have three fluorescence lifetimes (1.16, 45.25 and 267.63 ns, respectively), in strong contrast to the other three clusters (two short lifetimes, ~1.0 and ~2.3 ns, respectively, see Fig. S6), indicating that Au_{24} has different fluorescence mechanism compared with the other three clusters. Further efforts (including the resolution of the structure of Au_{24}) are needed to gain a deep understanding of the strong fluorescence of Au_{24}. Besides, that the maximum emissions of Au_{25}, Au_{38} and Au_{144} shift towards near IR (see Figure 3) compared with that of Au_{24} indicates their molecules have lower energy gaps than Au_{24} molecules between the lowest vibrational level of the first singlet and the ground state. The gap between the first oxidation and the first reduction potential revealed by DPV can provide some clues for that. Finally, it is worth mentioning that Au_{24} shows high photobleaching stability (see Fig.S7), which imparts Au_{24} an additional merit for practical application.

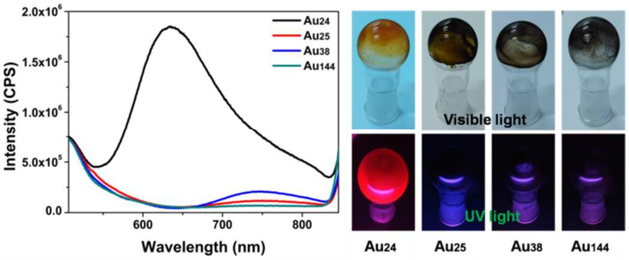


Fig. 3 Fluorescence spectra of $Au_{24}(SC_2H_4Ph)_{20}$ (black), $Au_{25}(SC_2H_4Ph)_{18}$ (red), $Au_{38}(SC_2H_4Ph)_{24}$ (blue) and $Au_{144}(SC_2H_4Ph)_{60}$ (dark cyan), respectively (Left), and digital photos of the four nanoclusters under visible and 365 nm UV light irradiation (right).

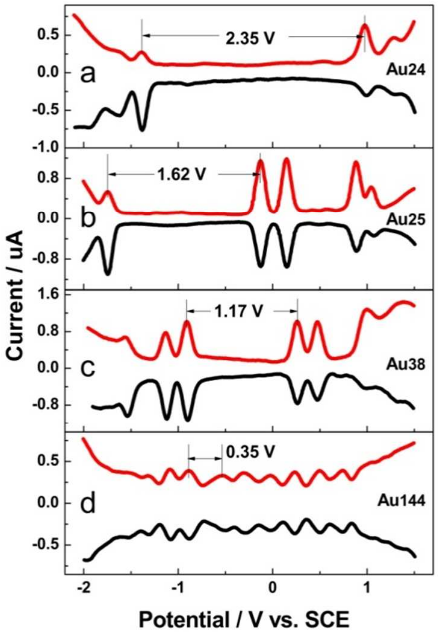


Fig. 4. Differential pulse voltammetry (DPV) of $Au_{24}(SC_2H_4Ph)_{20}$ (a), $Au_{25}(SC_2H_4Ph)_{18}$ (b), $Au_{38}(SC_2H_4Ph)_{24}$ (c) and $Au_{144}(SC_2H_4Ph)_{60}$ (d) at 10 $mV\cdot s^{-1}$ in degassed CH_2Cl_2 containing 0.1 M Bu_4NPF_6 (1 mm diameter Pt disk, SCE and carbon rod were used as working, reference and counter electrode, respectively)

In summary, a fluorescent gold nanocluster formulated as $Au_{24}(SC_2H_4Ph)_{20}$ was synthesized using a pseudo-AGR method and characterized by ESI-MS, TGA, DPV and fluorescence spectrometry. Specifically, DPV revealed that Au_{24} exhibits the largest gap between the first oxidation potential and the first reduction potential among the investigated phenylethanethiolated gold nanoclusters (including Au_{24}, Au_{25}, Au_{38} and Au_{144}). Phenylethanethiolated gold nanocluster with distinct fluorescence is rarely reported, thus our work has important implication for fluorescence study of metal nanoclusters. It is also expected that our work will stimulate more research on the development of some unique synthesis method for metal nanoclusters.

Acknowledgements

We greatly thank Dr. Meiling Wang for helpful discussions and assistance influorescence measurements. This work was supported by National Basic Research Program of China (Grant No. 2013CB934302), the Natural Science Foundation of China (No. 21222301, 21171170), the Ministry of Human Resources and Social Security of China, the Innovative Program of Development Foundation of Hefei Center for Physical Science and Technology (2014FXCX002), the CAS/SAFEA International Partnership Program for Creative Research Teams and the "Hundred Talents Program" of the Chinese Academy of Sciences.

Notes and references

1 R. Jin, *Nanoscale*, 2010, **2**, 343-362.
2 S. Choi, R. Dickson and J. Yu, *Chem. Soc. Rev.*, 2012, **41**, 1867-1891.
3 Y. Lu and W. Chen, *Chem. Soc. Rev.*, 2012, **41**, 3594-3623.
4 L. Shang, S. Dong and G. Nienhaus, *Nano Today*, 2011, **6**, 401-418.
5 J. Li, J. Zhu and K. Xu, *Trac-Trend. Anal. Chem.*, 2014, **58**, 90-98.
6 J. Zheng, C. Zhou, M. Yu and J. Liu, *Nanoscale*, 2012, **4**, 4073-4083.
7 H. Zhang, X. Huang, L. Li, G. Zhang, I. Hussain, Z. Li and B. Tan, *Chem. Commun.*, 2012, **48**, 567-569.
8 L. Zhang and E. Wang, *Nano Today*, 2014, **9**, 132-157.
9 Z. Luo, K. Zheng and J. Xie, *Chem. Commun.*, 2014, **50**, 5143-5155.
10 Z. Wu, M. Wang, J. Yang, X. Zheng, W. Cai, G. Meng, H. Qian, H. Wang and R. Jin, *Small*, 2012, **8**, 2028-2035.
11 M. Wang, Z. Wu, J. Yang, G. Wang, H. Wang and W. Cai, *Nanoscale*, 2012, **4**, 4087-4090.
12 S. Wang, X. Meng, A. Das, T. Li, Y. Song, T. Cao, X. Zhu, M. Zhu and R. Jin, *Angew. Chem. Int. Ed.*, 2014, **53**, 2376-2380.
13 Y. Yu, Z. Luo, D. Chevrier, D. Leong, P. Zhang, D.-e. Jiang and J. Xie, *J. Am. Chem. Soc.*, 2014, **136**, 1246-1249.
14 Z. Wu and R. Jin, *Nano Lett.*, 2010, **10**, 2568-2573.
15 C. Yao, J. Chen, M.-B. Li, L. Liu, J. Yang and Z. Wu, *Nano Lett.*, 2015, **15**, 1281-1287.
16 Z. Luo, X. Yuan, Y. Yu, Q. Zhang, D. Leong, J. Lee and J. Xie, *J. Am. Chem. Soc.*, 2012, **134**, 16662-16670.

17 Y. Chen, T. Yang, H. Pan, Y. Yuan, L. Chen, M. Liu, K. Zhang, S. Zhang, P. Wu and J. Xu, *J. Am. Chem. Soc.*, 2014, **136**, 1686-1689.
18 J. Sun and Y. Jin, *J. Mater. Chem. C*, 2014, **2**, 8000-8011.
19 L. Li, Z. Li, H. Zhang, S. Zhang, I. Majeed and B. Tan, *Nanoscale*, 2013, **5**, 1986-1992.
20 T. Rao, B. Nataraju and T. Pradeep, *J. Am. Chem. Soc.*, 2010, **132**, 16304-16307.
21 J. Xie, Y. Zheng and J. Ying, *J. Am. Chem. Soc.*, 2009, **131**, 888-889.
22 X. Yuan, Z. Luo, Q. Zhang, X. Zhang, Y. Zheng, J. Lee and J. Xie, *ACS Nano*, 2011, **5**, 8800-8808.
23 T. Rao and T. Pradeep, *Angew. Chem. Int. Ed.*, 2010, **49**, 3925-3929.
24 C. Huang, Z. Yang, K. Lee and H. Chang, *Angew. Chem. Int. Ed.*, 2007, **46**, 6824-6828.
25 C. Lin, T. Yang, C. Lee, S. Huang, R. Sperling, M. Zanella, J. Li, J. Shen, H. Wang, H. Yeh, W. Parak and W. Chang, *ACS Nano*, 2009, **3**, 395-401.
26 D. Lee, R. Donkers, G. Wang, A. Harper and R. Murray, *J. Am. Chem. Soc.*, 2004, **126**, 6193-6199.
27 M. Brust, J. Fink, D. Bethell, D. Schiffrin and C. Kiely, *J. Chem. Soc. Chem. Comm.*, 1995,**16**, 1655-1656.
28 Z. Wu, C. Gayathri, R. Gil and R. Jin, *J. Am. Chem. Soc.*, 2009, **131**, 6535-6542.
29 Z. Wu, M. MacDonald, J. Chen, P. Zhang and R. Jin, *J. Am. Chem. Soc.*, 2011, **133**, 9670-9673.
30 E. Shibu, M. Muhammed, T. Tsukuda and T. Pradeep, *J. Phys. Chem. C*, 2008, **112**, 12168-12176.
31 C. Zeng, T. Li, A. Das, N. Rosi and R. Jin, *J. Am. Chem. Soc.*, 2013, **135**, 10011-10013.
32 P. Nimmala and A. Dass, *J. Am. Chem. Soc.*, 2014, **136**, 17016-17023.
33 W. Kurashige, S. Yamazoe, K. Kanehira, T. Tsukuda and Y. Negishi, *J. Phys. Chem. Lett.*, 2013, **4**, 3181-3185.
34 Y. Shichibu, Y. Negishi, T. Tsukuda and T. Teranishi, *J. Am. Chem. Soc.*, 2005, **127**, 13464-13465.
35 S. Knoppe, A. Dharmaratne, E. Schreiner, A. Dass and T. Burgi, *J. Am. Chem. Soc.*, 2010, **132**, 16783-16789.
36 Z. Wu, *Angew. Chem. Int.Ed.*, 2012, **51**, 2934-2938.
37 M.-B. Li,S.-K. Tian, Z. Wu and R. Jin, *Chem. Commun.*, 2015, **51**, 4433-4436.
38 S. Tian, C. Yao, L. Liao, N. Xia and Z. Wu, *Chem. Commun.*, 2015, **51**, 11773-11776.
39 A. Das, T. Li, G. Li, K. Nobusada, C. Zeng, N. Rosi and R. Jin, *Nanoscale*, 2014, **6**, 6458-6462.
40 Y. Song, S. Wang, J. Zhang, X. Kang, S. Chen, P. Li, H. Sheng and M. Zhu, *J. Am. Chem. Soc.*, 2014, **136**, 2963-2965.
41 A. Das, T. Li, K. Nobusada, Q. Zeng, N. Rosi and R. Jin, *J. Am. Chem. Soc.*, 2012, **134**, 20286-20289.

TOC

An unexpected pseudo-AGR method was introduced to synthesize an unexpected fluorescent gold nanoclusters protected by phenylethanethiolate.