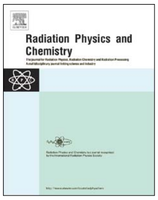
Radiation Physics and Chemistry ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem



Luminescence of Au(I)-thiolate complex affected by solvent

Lina Yang, Yuanjie Cao, Juan Chen, Zhihu Sun*, Tao Yao, Yong Jiang*, Shiqiang Wei

National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, PR China

HIGHLIGHTS

- Luminescent $[Au_{15}(SR)_{14-16}]^+$ complex is synthesized by dodecanethiol reducing $HAuCl_4$ in toluene.
- Non-luminescent $[Au_7(SR)_6]^+$ complex is yielded by the same synthesis in ethanol.
- The relationship between the luminescence intensity and solvent polarity is studied.
- Luminescence of Au(I)-SR complexes originates from aggregation of the bilayer supramolecular structures.
- Aggregation increases as solvent polarity decreases.

ARTICLE INFO

Article history:
Received 30 November 2015
Received in revised form
2 September 2016
Accepted 10 September 2016

Keywords:
Fluorescence
Au(I)-thiolate complex
Solvent effect
Aggregation
Supramolecular structures
Aurophilic interactions

ABSTRACT

This work presents a study on the correlation between luminescence property of Au(I)-SR (SR: thiolate) complexes and solvent polarity. Luminescent $[Au_{15}(SR)_{14-16}]^+$ complexes were synthesized in the weakly polar solvent of toluene, while the non-luminescent $[Au_7(SR)_6]^+$ species were obtained by the same synthesis method in the polar solvent of ethanol. The dependence of luminescence intensity on the mixed solvent with various toluene/ethanol ratios was also explored. It is proposed that the luminescence of Au(I)-SR complexes originates from the aggregation of the bilayer supramolecular structures induced by the weakly polar solvent. This aggregation strengthens the intra and intercomplex aurophilic $Au(I)\cdots Au(I)$ interactions and subsequently enhances the luminescence intensity of the complexes.

1. Introduction

In recent years, the luminescent Au nanoclusters (NCs) have become a subject of active research, owing to their promising applications in sensing and bioimaging (Chen et al., 2014; Das et al., 2015; Deng et al., 2016; Hsu and Lin, 2016; Sun et al., 2015; Wang et al., 2015). To design and synthesize strongly luminescent NCs products, understanding the origin of luminescence is important. Currently, the luminescence of ligand-covered gold NCs is widely interpreted to be a ligand-induced effect. For example, numerous reports suggest that the luminescence of thiolate (SR) capped Au NCs originates from the surface Au(I)-SR complexes, and the luminescence intensity is relevant to the charge transfer from S atom to the Au center. Zhang et al. reported that nearly 60% of gold atoms in their luminescent gold NCs were in the Au (I) state, which was responsible for the luminesce (Zhang et al., 2016). Li et al. (2013) found that the luminescence of polymer-capped Au NCs were associated with the Au(I) ions in the clusters. Besides, it is believed that the aggregation of Au(I)-SR complexes on metallic NCs cores could greatly enhance the fluorescence property of the products. Luo et al. reported that the controlled aggregation of Au(I)-SR complexes on the NCs surface is the source of the ultrabright luminescence of the as-obtained Au(0)@Au(I)-SR core-shell NCs (Luo et al., 2012). Cu(I)-SR complexes aggregated by Au(0) atoms were also shown by Kang et al. to be the active species for the strong fluorescence of the hybrid clusters (Kang et al., 2016). Considering that many Au(I)-SR complexes are fluorescent themselves, investigating their luminescent properties and the affecting effects will offer valuable information to understand the origin and tune the intensity of the luminescence of Au-SR NCs (Vanegas et al., 2016). Till date, comprehensive studies about luminescent Au(I)-SR complexes are still limited. Previous works have shown that both the types of ligands (Forward et al., 1995) and the length of alkyl chains (Cha et al., 2007) affect the luminescence of the Au(I)-SR complexes. For the aforementioned aggregation-induced emission of Au(0)@Au(I)-SR core-shell NCs (Luo et al., 2012), the aggregation extent is strongly dependent on the solvent, and thus solvent plays a critical role in determining the

---

* Corresponding authors.
E-mail addresses: zhsun@ustc.edu.cn (Z. Sun), hanyanjy@ustc.edu.cn (Y. Jiang).

http://dx.doi.org/10.1016/j.radphyschem.2016.09.013
0969-806X/© 2016 Elsevier Ltd. All rights reserved.

Please cite this article as: Yang, L., et al., Luminescence of Au(I)-thiolate complex affected by solvent. Radiat. Phys. Chem. (2016), http://dx.doi.org/10.1016/j.radphyschem.2016.09.013

luminescence properties of the aggregated NCs. Therefore, understanding how solvents affect the luminesce property of Au(I)-SR complexes could contribute to the better synthesis of luminescent gold NCs.

Herein, we prepared the luminescent Au(I)-SR complexes in the weakly polar solvent of toluene and identified their atomic composition by MALDI mass spectra. In contrary, in the polar solvent of ethanol, non-luminescent Au(I)-SR complexes were yielded by using the otherwise same synthesis method. The dependence of luminescence intensity on the mixed solvent with various toluene/ethanol ratios was also explored. A scenario involving the aggregation of the bilayer supramolecular structures of Au(I)-SR complexes is invoked to interpret the solvent-polarity dependent luminescence of the complexes.

2. Experimental section

Sample preparations: The Au(I)-SR complexes were prepared by reaction of gold salt with excess dodecanethiol ($C_{12}SH$) in pure toluene, ethanol, or mixed toluene/ethanol solvents with different volume fractions of toluene. Simply, 30 μL dodecanethiol (0.125 mmol) was dropped into a solution of $HAuCl_4 \cdot 4H_2O$ (0.0243 mmol) in the solvent (5 ml). After stirring at room temperature for 3 h, the mixture was subjected to subsequent characterizations.

Materials Characterizations: The UV–vis absorption spectra were recorded in transmission mode with UV–vis light perpendicular to the incident X-ray beam. A Purkinje General TU-9001 spectrometer was used to collect the UV–vis absorption data in the wavelength range of 300–800 nm, and the background absorption was corrected using the corresponding toluene/ethanol solvent employed in the synthesis of the complex. Matrix-assisted laser desorption ionization mass-spectrometry (MALDI-MS) measurements were performed with a Bruker Autoflex III mass spectrometer in positive linear mode. The aliquots were extracted from the reaction flask and then mixed with matrix trans-2-[3-(4-tert-butylphenyl) – 2-methyl-2-propenyldidene] malononitrile (DCTB) in the ratio of ~1:1000. During the measurements, the laser pulse intensity was kept as low as possible to prevent production of fragments. The photoluminescence (PL) were performed by FLUOROLOG-3-TAU fluorescence spectrometer equipping with an integrating sphere.

3. Results and discussions

The brightest luminescent Au(I)–SR complexes were obtained by reaction of $HAuCl_4 \cdot 4H_2O$ with excess $C_{12}SH$ in the solvent of pure toluene. Upon adding $C_{12}SH$, the solution turned from light yellow to dark yellow in a few minutes. After stirring the mixture for 3 h, the yellowish color disappeared completely and the solution became white (the inset in Fig. 1(a)), which is the typical color of Au(I)-SR complexes (Cha et al., 2007). The atomic compositions of the Au(I)-SR species were further characterized by MALDI-MS as shown in Fig. 1(b). It displays many peak groups, with the largest group being $[Au_{15}(SR)_2S_{12-14}]^+$($m/z$=3742–3806). Although we used laser pulse intensity as low as possible during the MALDI-MS measurements, production of fragments of the complexes was still unavoidable. The three peaks associated with the denotation $[Au_{15}(SR)_2S_{12-14}]^+$ are ascribed to the $[Au_{15}(SR)_2S_{12}]^+$, $[Au_{15}(SR)_2S_{13}]^+$ and $[Au_{15}(SR)_2S_{14}]^+$ species, where the

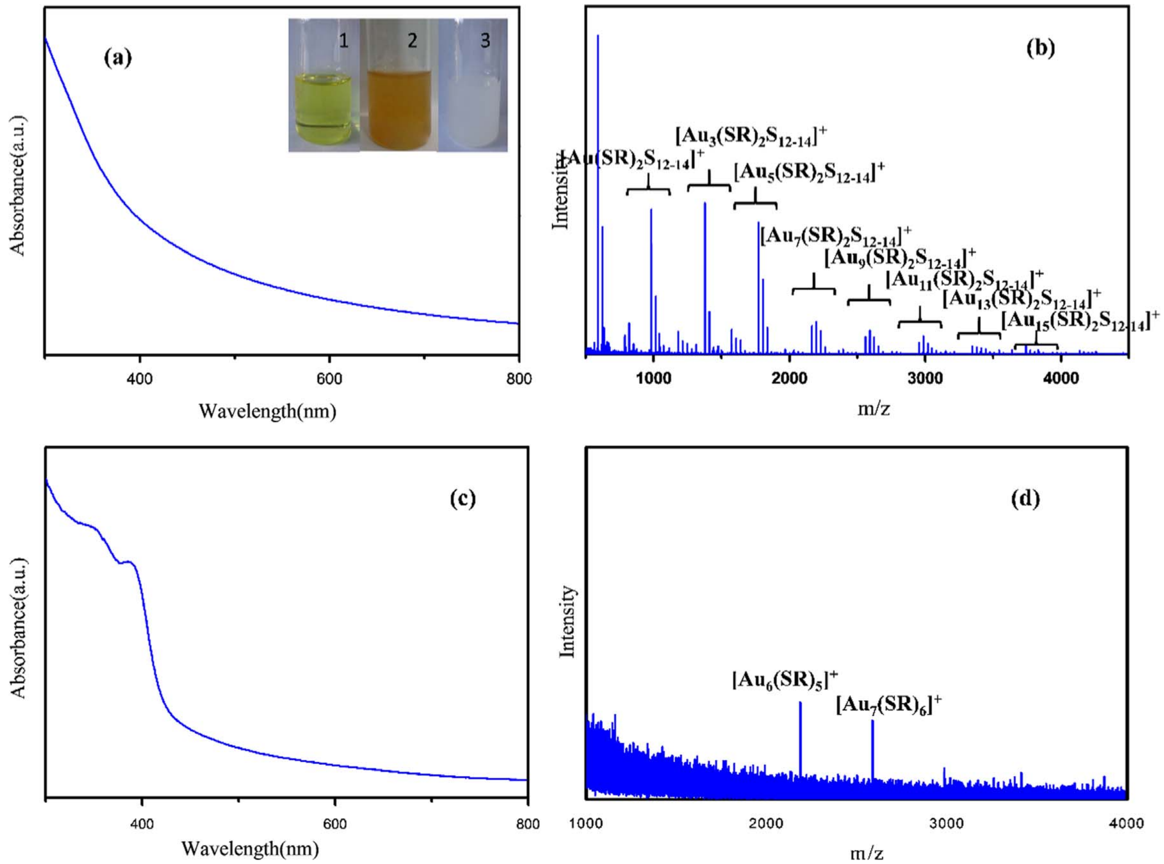


Fig. 1. (a) UV–vis absorption spectra and (b) MALDI mass spectrum of the Au(I)-$SC_{12}H_{25}$ complexes in toluene. The mass spectrum shows the small groups of $[Au_n(SR)S_m]^+$. For example, the three peaks associated with the label $[Au_{15}(SR)_2S_{12-14}]^+$ are a mixture of $[Au_{15}(SR)_2S_{12}]^+$, $[Au_{15}(SR)_2S_{13}]^+$ and $[Au_{15}(SR)_2S_{14}]^+$(R=$C_{12}H_{25}$-). (c) UV–vis absorption spectra and (d) MALDI mass spectrum of Au(I)–$SC_{12}H_{25}$ in ethanol.

Please cite this article as: Yang, L., et al., Luminescence of Au(I)-thiolate complex affected by solvent. Radiat. Phys. Chem. (2016), http://dx.doi.org/10.1016/j.radphyschem.2016.09.013