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Electrogenerated Chemiluminescence of Gold Nanoclusters

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Graduate Program in Chemistry

A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy

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Electrogenerated Chemiluminescence of Gold Nanoclusters

by

Mahdi Hesari

Graduate Program in Chemistry

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

The School of Graduate and Postdoctoral Studies The University of Western Ontario London, Ontario, Canada

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Abstract

A series of monodispersed AuNCs (size < 2 nm) including Au$_{144}$(SR)$_{60}$, Au$_{38}$(SR)$_{24}$ and Au$_{25}$(SR)$_{18}$ (z =1-, 0 and 1+, SR=2-phenylethanethiol) were prepared. All these nanoclusters showed molecule-like optical and electrochemical properties. These two features are essential for an electrogenerated chemiluminescence or electrochemiluminescence (ECL) study. The Au$_{144}$(SR)$_{60}$ showed a small HOMO-LUMO gap determined by electrochemistry. No ECL light was seen in the annihilation process, while NIR ECL was observed with tri-$n$-propylamine (TPrA) (Chapter 2). ECL was highly efficient in the Au$_{38}$(SR)$_{24}$/TPrA co-reactant system. This nanocluster also showed ECL emission with benzoyl peroxide (BPO), while no ECL was detected in the annihilation route (Chapter 3). The ECL of Au$_{25}$(SR)$_{18}$ (z =1-, 0 and 1+) were discovered to emit NIR ECL light in the presence of either TPrA or BPO co-reactant. The Au$_{25}$(SR)$_{18}$+/ TPrA system revealed the strongest ECL emission among the three Au$_{25}$ oxidation states (Chapter 4). The thermodynamic (Latimer-type diagram) and the kinetic origins of Au$_{25}$(SR)$_{18}$ ECL were explored in the presence of TPrA (Chapter 5). And lastly, the NIR ECL of Au$_{25}$(SR)$_{18}$− nanoclusters was mechanistically investigated in the presence of both TPrA and BPO with NIR emissions in both systems (Chapter 6).

In each case multiple ECL emissions were observed. The ECL peak wavelength and ECL intensity can be tuned by means of both the co-reactant concentration and applied electrode potential. It is worth noting that the Au$_{38}$(SR)$_{24}$ showed the strongest ECL efficiency among all the clusters studied, and the Au$_{25}$(SR)$_{18}$ clusters possessed a rich photoelectrochemistry leading to highly efficient ECL.
Keywords

Electrochemistry, Electrogeminated chemiluminescence, Electrochemiluminescence, ECL efficiency, Spooling spectroscopy, *In-situ* spectroelectrochemistry, Gold nanoclusters, Au$_{25}$,(SR)$_{18}$, Au$_{38}$,(SR)$_{24}$, Au$_{144}$,(SR)$_{60}$, Tri-*n*-propylamine (TPrA), Benzoyl peroxide (BPO).
Dedication

This work is dedicated to the memory of my father
to my family
and
my wife
Acknowledgments

I would like to take this opportunity to express my gratitude and appreciation to Dr. Mark S. Workentin, for his patience, support, and supervision through these years. I would like to thank Dr. Zhifeng Ding for his continued guidance and insightful comments that have helped me in getting my thesis in the present form. It has been a great pleasure working with and learning from both of them.

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<th>Definition</th>
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<tr>
<td><strong>Roman Alphabet</strong></td>
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</tr>
<tr>
<td>A</td>
<td>amperes or Amps</td>
</tr>
<tr>
<td>Abs</td>
<td>absorbance</td>
</tr>
<tr>
<td>ACN</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>A.U.</td>
<td>arbitrary unit</td>
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<tr>
<td>BPO</td>
<td>benzoyl peroxide</td>
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<td>°C</td>
<td>degrees Celsius</td>
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<tr>
<td>CCD</td>
<td>charge-couple device</td>
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<tr>
<td>CDCl₃</td>
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<tr>
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<td>density functional theory</td>
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<tr>
<td>DPV</td>
<td>differential pulse voltammetry</td>
</tr>
<tr>
<td>E</td>
<td>voltage (V)</td>
</tr>
<tr>
<td>E°</td>
<td>standard potential (V)</td>
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<tr>
<td>E°'</td>
<td>formal potential (V)</td>
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<tr>
<td>ECL</td>
<td>electrognerated chemiluminescence or electrochemiluminescence</td>
</tr>
<tr>
<td>Abbreviation</td>
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<tr>
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<tr>
<td>$E_{ox}^{o+}$</td>
<td>formal oxidation potential (V)</td>
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<td>$E_{red}^{o+}$</td>
<td>formal reduction potential (V)</td>
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<tr>
<td>$E_p$</td>
<td>peak potential (V)</td>
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<td>Eq.</td>
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<td>eV</td>
<td>electronvolt</td>
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<td>Fc</td>
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<td>Fc$^+$</td>
<td>ferrocnium cation</td>
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<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
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<tr>
<td>LUMO</td>
<td>lowest occupied molecular orbital</td>
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<tr>
<td>MALDI</td>
<td>matrix-assisted laser desorption/ionization</td>
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<tr>
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</tr>
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<td>mmol</td>
<td>millimole</td>
</tr>
<tr>
<td>MPN</td>
<td>metal protected nanoparticle</td>
</tr>
<tr>
<td>MS</td>
<td>mass spectrometry</td>
</tr>
<tr>
<td>$n$</td>
<td>number of electrons transferred</td>
</tr>
<tr>
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<td>nanoamp</td>
</tr>
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<td>NIR</td>
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<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>PL</td>
<td>photoluminescence</td>
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PMT  photomultiplier tube

ppm  part per million

$[\text{Ru(bpy)}_3]^{2+}$  tris(2,2'-bipyridine) ruthenium (III)

SCE  saturated calumel electrode

SEC  spectroelectrochemistry

TBABr  tetra-$n$-butylammonium bromide

TEM  transmission electron microscopy

THF  tetrahydrofuran

TOABr  tetra-$n$-octylammonium bromide

TPrA  tri-$n$-propylamine

UV  ultraviolet

Vis  visible

**Greek Alphabet**

$\Delta H^\circ_{\text{ann}}$  enthalpy change of ion annihilation (eV)

$\lambda$  wavelength (nm)

$\mu$  micro
Chapter 1

1 Introduction and Overview

1.1 Gold Nanoparticles

The rapid transition from the science of “colloidal gold” to the chemistry of “gold nanoclusters” in the past few decades indicates the growing importance of gold nanomaterials beyond their traditional usage. Since ancient times, the synthesis of colloidal gold has been important. In 4th century A.D. a dichroic glass was carved (Lycurgus cup) which displayed various colors, depending on the direction of light that irradiated it. In the 17th century, glass-coloring involved the use of a ruby-color gold solution to produce a rich red colorant. This process was also used in staining glass; scientifically documented by Faraday in the 1850s. The process was based on the reduction of a gold salt using phosphorous, which eventually formed gold colloids that were estimated to be between 50-100 nm. These gold colloids appeared in the red-blue color range depending on their size, with the smaller sizes resulting in a deeper red solution. Despite their long history of use, they were not documented as being Au nanoparticles until 1951, when Turkevich developed a new gold material via a simpler synthetic method. He produced smaller particles in the size range of 10-20 nm measured by electron microscopy. This generation showed smaller size distribution, but were still polydispersed, therefore named as “nanoparticle” or “small-particle”. Using the Turkevich method, nanoparticles were produced by the reduction of an aqueous solution of a gold (III) salt in the presence of sodium citrate, while the solution was heated to boiling. The spherical nanoparticles were stabilized through the negative charge provided by the citrate anions, which made them water-soluble. The reduced metallic cores in this traditional protocol are relatively weakly stabilized. Interestingly, the size of the final product(s) could be tuned by changing the ratio of gold (III) salt to citrate salt or by varying the heating temperature. The smaller gold nanoparticles could be visually identified due to their ruby coloring, while the larger particles pertain a blue color. These
types of nanoparticles have been utilized extensively, especially with protocols to change the protecting ligands via a place exchange. In 2013 the Turkevich method was later modified by Navarro, who used sodium acetylacetonate prior to the addition of sodium citrate. The acetylacetone forms a complex and reduces Au(III) to Au(I), followed by the reduction of Au(I) to Au⁰ by the sodium citrate, which leads to less polydisperse products. Navaro’s method produced nanoparticles decorated with a water-soluble copolymer for bio-imaging and photodynamic therapy.

The most significant breakthrough in this area since the Turkevich’s report was not until 1994, when Brust, Walker, Bethell, Schiffrin, and Whyman described a methodology (known as the Brust-Schiffrin method) to produce much smaller gold nanoparticles in the range of 1-3 nm, which were protected (stabilized) by aliphatic thiolates. The use of thiolates provided additional stability of these nanoparticles due to the stronger Au-S intermediates (compared to the citrate). More importantly, the structural diversity, due to the use of organic thiolates (for example see R functionality in Scheme 1.1 and 1.2) as the capping ligand, initiated a new research on the nanoparticles. Specifically, these gold nanomaterials, also called monolayer protected nanoparticles (MPN), are synthesized using the Brust-Schiffrin method, in which gold (III) salt transfers from an aqueous phase to an organic phase (toluene) and then mixes with 1:1 of thiol to gold ratio (protecting ligand; $\text{C}_{12}\text{H}_{25}\text{SH}=1$-dodecanethiol). The resulting -(Au(I)-SR-Au(I)-SR)- intermediate is reduced to the metallic nanoparticles using a reducing agent such as sodium borohydride (Scheme 1.1).
Scheme 1.1 Illustration of (two-phase) Brust-Schiffrin method through nanoparticle synthesis and place-exchange reaction.

This protocol has been a benchmark now for many years to make MPNs protected with a wide range of organothiolate ligands, which induce a variety of important catalytic, optical-electrochemical, and chemical properties on the metallic core (vide infra). The advantage of this generation of nanoparticle is that the primary protecting ligand(s) can be varied easily using different initial protecting thiolate or via a "place-exchange" reaction. In a typical place-exchange reaction, a higher mole ratio of the desired thiol reacts with the previously prepared nanoparticles, resulting in ligand substitution (Scheme 1.2).
Many research groups, motivated by the work of Brust et al., worked towards synthesis procedures to reduce the polydispersity of the final products with hopes of finding an optimized synthetic protocol to easily create and characterize monodispersed Au nanoclusters (AuNCs). The reaction temperature, initial gold to thiol ratio, the nature of the organothiolate and other variables have significant impacts on the MPN. For example, the average MPN product size can be varied from about 5 nm down to 1 nm by altering the gold to thiolate ratio. Also, the inherent properties of those alkylthiolate or
arylthiolate ligands dictate the solubility of MPNs in moderately polar to nonpolar media, but not water. Solubility properties are important to lessen the MPN product’s size polydispersity. Whetten et al. employed the Brust-Schiffrin method and the gold to thiol ratio changed from 1:1 to 1:2. The isolated products were characterized by high resolution electron microscopy (HREM), mass spectrometry, and powder X-ray diffraction (PXRD) indicating narrow size distribution with the composition of Au79, Au140, (Au225), Au314 and Au459. They found that increases in the gold to thiol ratio could affect the monodispersity of the MPNs towards the less polydisperse product(s).

Interestingly, this had also been accomplished much earlier. For example, in 1981 Mingos and co-workers successfully synthesized a gold “cluster” with the formula of [Au13(PMe2Ph)10Cl2](PF6)3, which has been previously predicted through a general theoretical analysis. It is worth noting that a wide range of other metals have been used to produce “small-particles”, in which the size regime was <1 nm to ~10 nm. Furthermore, the researchers were exploring physicochemical properties of clusters and colloids, which were made of Ag, Cu, Pb or Cd. This approach has also been used recently, resulting in the formation of other gold clusters constructed with phosphorous derivatives.

To overcome the problem associated with the polydispersity several synthetic modifications have been tried. The first breakthrough in the realm of nanocluster research was carried out by Murray and co-workers who introduced a modification of the general Brust-Schiffrin (two-phase) methodology. For example, instead of two-phase reactions, a one-phase reaction using tetrahydrofuran (THF) as solvent was tested, in which lithium triethylborohydride was used as the reducing agent. These changes resulted in two products, namely Au140(SR)53 and Au38(SR)24 nanoclusters in 2:1 ratio. Later, matrix assisted-laser desorption/ionization (MALDI) showed that the actual composition of the former nanoclusters was indeed Au144(SR)60. Much work was done using the new protocols and indeed Au38(SR)24 was shown to be actually Au25(SR)18.TOA (Au25−, TOA=(CH3(CH2)7)4N+). The latter was confirmed unambiguously once single crystal(s) was prepared to allow for X-ray analysis. Later, it was shown that Au38 decorated with 24
thiolate ligand was prepared (using two step procedure, *vide infra*) with distinguishable optical and electrochemical features from the original Au25(SR)18.TOA nanoclusters. This better understanding of the synthesized Au25(SR)18.TOA and Au38(SR)24 nanoclusters was obtained using X-ray crystallography, which provided precise details on the single crystal structure of these gold nanoclusters.19-21 This so-called Au25(SR)18.TOA “cluster” consists of a 13 member gold core and 6 dimeric -(Au2(SR)3) “staple motifs” which formed a semi-ring around the gold core (Figure 1.1B). It is worth noting that Au38 has a Au23 core decorated with three -(Au(SR)2)- and six dimeric staples -(Au2(SR)3 (Figure 1.2). Jin and co-workers successfully correlated the Au25(SR)18.TOA crystal structure to its UV-Vis spectroscopy.20 The Au25 has three main distinct UV-Vis peaks at 400, 460 and 680 nm. The theoretical calculations along with the crystal structure determined that the absorption is related to the HOMO-LUMO gap with 1.3 eV energy difference. The other two experimentally observed optical peaks are originated from HOMO to LUMO+1, LUMO+2 (peak at 460 nm) and HOMO-5 to LUMO (peak at 400 nm) (Figure 1.1).
Jin’s group has expanded the one-phase synthesis used by Murray under kinetic control to produce the monodispersed Au$_{25}$(SR)$_{18}$ as the main product. In this protocol the reaction mixture (gold salt and thiol) was cooled to 0°C to control the aggregation of the -(-Au$^{1}$-SR-Au$^{1}$-SR-)$_n$ intermediate formation.$^{22}$ Based on this protocol they have prepared a wide range of Au$_{25}$(SR)$_{18}$ clusters using different protecting thiol ligands (such as HS-(CH$_2$)$_{11}$CH$_3$, phenylethanethiol, glutathione). The synthesis of Au$_{25}$(SR)$_{18}$ clusters performed in the presence of a counter ion and absence of oxygen showed that these...
parameters affect the yield and the ultimate oxidation state of the final product.\textsuperscript{23} Interestingly, the presence or absence of a counter ion in the (direct) synthetic procedure can alter the charge state of the \( \text{Au}_{25}(\text{SR})_{18} \) nanoclusters. For example, in the presence of tetra-\( n \)-octylammonium bromide (TOABr), the \( \text{Au}_{25}(\text{SR})_{18}.\text{TOA} (\text{Au}_{25}^{-}) \) was the major product, while in the absence of TOABr, the \( \text{Au}_{25}(\text{SR})_{18} (\text{Au}_{25}^{0}) \) was obtained.\textsuperscript{22} So far there has been no report of the direct preparation of \( \text{Au}_{25}(\text{SR})_{18}^{+}X^{-} (X= \text{C}_{6}\text{F}_{5}\text{CO}_{2}^{-} \text{or BF}_{4}^{-}) \), although it has been prepared using different chemical-electrochemical protocols using either \( \text{Au}_{25}^{-} \) or \( \text{Au}_{25}^{0} \) nanoclusters as the starting material.\textsuperscript{24-25} It has also been shown that the solvent,\textsuperscript{26} the gold to thiol ratio and reduction rate\textsuperscript{27-28} play important roles on the yield, monodispersity, size and composition of the gold nanoclusters. For example, using THF, acetone or ethyl acetate \( \text{Au}_{25}(\text{SR})_{18} \) is the major product, while in methanol or acetonitrile \( \text{Au}_{144}(\text{SR})_{60} \) and larger nanoparticles formation is favorable, likely due to the influence of solvents on the Au-SR intermediate.\textsuperscript{26}

The \( \text{Au}_{38}(\text{SR})_{24} \) was subsequently prepared via a two-step synthesis protocol. The synthesis consisted of two stages. First, \( \text{Au}_{n}(\text{SG})_{m} (\text{SG} = \text{glutathiolate}) \), where \( n \) ranging from 38 to \( \sim 102 \) was prepared via reduction of the \( (-\text{Au}^{1}\text{-SG-Au}^{1}\text{-SG}-)_n \)-intermediate. Second, the \( \text{Au}_{n}(\text{SG})_{m} \) intermediate was reacted with high excess of neat thiol ligand while heating for several hours.\textsuperscript{29} The final product was characterized using mass spectrometry and the cluster composition was \( \text{Au}_{38}(\text{SR})_{24} \) which is fairly stable. This cluster also revealed distinct optical and electrochemical properties. The experimental HOMO-LUMO gap estimations based on the UV-Vis spectroscopy and differential pulse voltammetry \textit{ca}. 0.9 eV\textsuperscript{30} showed a good agreement with that calculated by H"{a}kkinen.\textsuperscript{31} Importantly, the crystal structure of \( \text{Au}_{38} \) determined by Jin and coworkers revealed that it consists of a core-shell construction. The core is made of 23 gold atoms, two fused \( \text{Au}_{13} \) (icosahedral) sharing a common \( \text{Au}_{3} \) face, while the shell showed consists of three monomeric \( \text{Au}(\text{SR})_{2} \) staples and six dimeric staples \( \text{Au}_{6}(\text{SR})_{3} \) (Figure 1.2).\textsuperscript{21} Interestingly, this cluster also showed chiral properties because of the original crystal structure.\textsuperscript{21,31}
Later, the chiral properties of $\text{Au}_{38}(\text{SR})_{24}$ were enhanced by replacing the original ligands with chiral ligands such as bidentate, axially chiral 1,1′-binaphthyl-2,2′-dithiol (BINAS) via place exchange reaction, as described in an extensive study by Bürgi and co-workers.\textsuperscript{32-33} Recently, Jin and his research group showed that $\text{Au}_{38}$ clusters can be used as a precursor to produce $\text{Au}_{36}$ under thermal conditions (reflux) in the presence of excess of tertbutylbenzene thiol.\textsuperscript{34} The $\text{Au}_{38}$ to $\text{Au}_{36}$ transformation involves four steps: (I) formation of $\text{Au}_{38}(\text{SR})_{24}(\text{SR'})_x$, where $x < 12$, (II) transformation of $\text{Au}_{38}(\text{SR})_{24}(\text{SR'})_x$ to $\text{Au}_{36}(\text{SR})_{24}(\text{SR'})_x$, (III) reconstruction/transformation of new cluster along with formation of $\text{Au}_{40}(\text{SR})$, and (IV) production of $\text{Au}_{36}(\text{SR'})_{24}$.\textsuperscript{35} The crystal structure of $\text{Au}_{36}(\text{SR})_{24}$ showed a completely different framework relative to $\text{Au}_{38}(\text{SR})_{24}$ with an $\text{Au}_{28}S_{12}$ member gold-sulfur core, which is covered with four $\text{Au}(\text{SR})_2$ staple motifs (Figure 1.3).
Figure 1.3 (A) Core-shell crystal structure, and (B) shows FCC kernel core of the Au\textsubscript{36}(SR)\textsubscript{24}. Reprinted with permission from ref 34. Copyright 2012 Wiley.

The nature of the protecting thiolate ligand and also synthetic technique can alter the size, shape and composition of gold clusters. The inherent properties of the organothiolate ligands have been exploited to produce a wide range of gold clusters. For example, Au\textsubscript{25}(SR)\textsubscript{18} nanoclusters with e.g. R= glutathione or captopril showed different properties such as solubility in water.\textsuperscript{36-37} It has been proposed by Hӓkkinen and co-workers that using a bulky organothiolate ligand would thermodynamically favor the formation of small gold clusters, such as Au\textsubscript{19}(SR)\textsubscript{12}.\textsuperscript{38} Thus, many efforts have been made to use different bulky ligands with various structural properties to prepare novel Au clusters. For example, Nishigaki et al. used 2,6-diphenylbenzenethiol (DppSH) in the Au\textsubscript{25} synthesis, resulting in the formation of Au\textsubscript{25}(DppS)\textsubscript{11} clusters. The further structural analysis revealed that the cluster structure is twisted mainly due to use of this bulky ligand. In this case, although the cluster size and composition of Au\textsubscript{25} are preserved, the number of ligands and core construction was altered significantly.\textsuperscript{39}
The structure for \( \text{Au}_{25}(\text{DppS})_{11} \) is shown in Figure 1.4, where its high resolution X-ray diffraction (HRXRD) is comparable with that of \( \text{Au}_{25}(\text{SR})_{18} \). Surprisingly, there is no core-shell evidence similar to the observed structure in \( \text{Au}_{25}(\text{SR})_{18} \) (\textit{vide supra}), while the same electronic structure has been proposed for \( \text{Au}_{25}(\text{DppS})_{11} \). Some other bulky thiols (\textit{e.g.} adamantanethiol or cyclohexanethiol) have been used in a typical two-phase Brust-Schiffrin reaction with 10:1 thiol to gold ratio. The resulting purified clusters showed a broad range of compositions including \( \text{Au}_{30}(\text{SAd})_{18} \), \( \text{Au}_{39}(\text{SAd})_{23} \), \( \text{Au}_{65}(\text{SCy})_{30} \), and \( \text{Au}_{67}(\text{SCy})_{30} \), each characterized using MALDI-TOF mass spectrometry. Interestingly, no \( \text{Au}_{25}(\text{SAd})_{18} \) was detected through the study, which proposed to be an effect of the bulky ligands on changing the Au cluster’s composition.40 Dass and co-workers used the adamantanethiol along with \textit{tert}-butylthiol using a two-step synthetic protocol with lower thiol to gold ratio (3:1). The mass spectroscopic analysis proposed a new class of small gold clusters with formula \( \text{Au}_{30}(\text{SR})_{18} \). They also showed that the use of adamantanethiol can lead to the formation of similar gold clusters.41 Later, they succeeded in determining the crystal structure of \( \text{Au}_{30}(\text{S-$t$-Bu})_{18} \), revealing a gold-thiolate protecting layer which consists of a bridging SR-groups, as well as monomeric \( \text{Au}(\text{S-$t$-Bu})_{2} \) and trimeric \( \text{Au}_{3}(\text{S-$t$-Bu})_{4} \) units (Figure 1.5).42 They found that this cluster shows circular dichroism (CD) as seen in \( \text{Au}_{38}(\text{SR})_{24} \).
Recently, Jin’s group also employed cyclohexanethiol in one- and two-phase synthetic methods, which ended up with the formation of two novel Au clusters with stoichiometry of \( \text{Au}_{23}(\text{SR})_{17} \text{TOA} \) and \( \text{Au}_{64}(\text{SR})_{32} \).\(^{0,43-44} \) In these cases, although the same ligand has been used, the synthesis method played an important role in the final product formation. We succeeded in synthesizing and isolating \( \text{Au}_{23}(\text{SR})_{17} \text{TOA} \), where the gold cluster was decorated with tert-butylthiol through a one-phase/ one-step protocol.\(^{44} \) The products were isolated via solvent extraction using acetonitrile and dichloromethane. This work is not included in the thesis. The solvent used in the synthesis procedure alters the ratio of the product(s). In other words, the properties of the solvent affect the monodispersity of the desired nanocluster(s), as shown for the synthesis of \( \text{Au}_{25}(\text{SR})_{18} \) and \( \text{Au}_{144}(\text{SR})_{60} \) in different solvent such as tetrahydrofuran, acetonitrile, acetone, ethyl acetate and methanol.\(^{26} \) Lastly, the rate of the reducing agent addition (e.g. sodium borohydride) changes the cluster composition as reported for \( \text{Au}_{20}(\text{SR})_{16} \) and \( \text{Au}_{24}(\text{SR})_{20} \).\(^{27-28} \) These two clusters were synthesized using the same protocol (two-phase/Brust-Schiffrin), while the rate of NaBH\(_4\) addition changed from drop-wise (\( \text{Au}_{24}(\text{SR})_{20} \)) to slow addition (\( \text{Au}_{20}(\text{SR})_{16} \)).
Methods are now available for producing stoichiometric metallic-like nanoclusters with the hope of expanding featured applications. One can conclude that the main factors for tuning the size, composition and monodispersity of gold nanoclusters are the thiol structural properties, gold to thiol ratio, solvent and reducing agent addition rate.

1.1.1 Distinct properties of the Au clusters

As the synthesis of various gold nanoclusters is better understood, more efforts are being directed to understanding their structural properties and use them in applications.

1.1.1.1 Catalytic properties of gold nanoclusters

Applications of metal nanoparticles, including gold nanoparticles and nanoclusters, have been extensively exploited in catalytic processes, due to the high exposed Au surface area. Reports about the applications of gold nanoclusters expand the use of the most studied Au$_{25}$(SR)$_{18}$ nanoclusters in both oxidative and reductive catalysis reactions. This nanocluster has also been employed in the electrocatalytic reactions in the presence of different substrates such as benzoyl peroxides and 2-benzonitrile derivatives. Importantly, Au$_{25}$(SR)$_{18}$ nanoclusters are utilized in an efficient electrocatalytic process where CO$_2$ is reduced to CO. It is a very important conversion because CO$_2$ is not only an important greenhouse gas, but also represents an abundant starting material for the generation of fine chemicals and fuels. Other gold clusters such as Au$_{38}$(SR)$_{24}$ are also now used in catalytic reactions.

1.1.1.2 Electrochemical properties

Murray’s group was the first to discover that large gold nanoparticles, decorated by alkylthiols, have quantized charge electrochemical properties, which were promising as multi-electron donor/acceptor reagents and catalysts. Their Science paper in 1998 on the
study the electrochemistry of “molecule-like” gold nanoclusters in the range of 8 to 38 kilodaltons (KDa) core mass with size range of 1.1 to 1.9 nanometers in diameter was a great achievement in the field of gold nanoparticle electrochemistry. They showed that the smaller gold clusters with ~ 8KDa mass unit (later assigned as Au$_{25}$(SR)$_{18}$) revealed well-defined differential pulse voltammograms (DPVs) with a clear HOMO-LUMO gap (Figure 1.6). The larger nanoparticles assigned as Au$_{147}$ showed a multiple redox activity. Later, Quinn and co-workers did a precise electrochemical analysis on these clusters identifying at least 15 detectable redox couples. These nanoparticles were further precisely characterized as Au$_{144}$(SR)$_{60}$ using MALD-TOF mass spectrometry.
Figure 1.6 Differential pulse voltammograms of different size gold clusters with 8-38 KDa mass units. Reprinted with permission from ref 10. Copyright 1998 The American Association for the Advancement of Science.

In 2004, Murray’s group further developed a synthetic method (following the Brust-Shiffirin reaction) to prepare the Au_{25}(SR)_{18} (vide supra) (although they initially misidentified it as the Au_{38}(SR)_{24}).\textsuperscript{17} They studied the electrochemical behaviors of the final purified product, showing similar features as that reported for 8 KDa fraction (Au_{25}(SR)_{18}) (Figure 1.6). The HOMO-LUMO gap can be calculated from the first
oxidation and reduction peak potential values. The Murray group also proposed that there would be a charge correction value of 0.3 eV due to the intra-cluster charge transfer at the metal-core-molecular-layer interface. In 2008, the single crystal structure of Au_{25}(SR)_{18} cluster was determined by the Murray and then Jin’s groups.\textsuperscript{19-20,58} Then, the estimations for the diffusion coefficient of the wrongly named Au_{38}(SR)_{24} turned to be incorrect.\textsuperscript{58} Au_{38}(SR)_{24} nanoclusters synthesized by Qian et al.\textsuperscript{29-30} had different electrochemical behaviors from Au_{25}’s.\textsuperscript{30, 60} (Updated details can be found in Chapter 3 of this thesis). There are also reports on the electrochemical behavior of other small gold clusters such as Au_{130}(SR)_{50},\textsuperscript{61} Au_{64}(SR)_{32},\textsuperscript{43} Au_{30}(SR)_{23},\textsuperscript{41} Au_{24}(SR)_{20},\textsuperscript{62} Au_{23}(SR)_{17},\textsuperscript{45} and Au_{20}(SR)_{16}.\textsuperscript{62}

1.1.1.3 Optical properties

Different spectroscopic techniques such as ultraviolet visible (UV-Vis) absorption spectrometry and photoluminescence (PL) spectroscopy have been used to characterize the optical properties of the various Au nanoclusters and to correlate the structures to electronic configurations. Interestingly, the majority of the aforementioned Au nanoparticles/clusters have shown absorption and photoluminescence properties with distinct features, which can be used as an optical fingerprint. As shown in Figure 1.7, the isolated large nanoparticles with size >5 nm (panel A) reveal a plasmonic absorbance at \textit{ca.} 500 nm (depends on size), while medium size nanoparticles (size ~ 1.7 nm, panel B) show a band around 520 nm. Furthermore, Au nanoclusters display more optical features compared to the large ones (Figure 1.7 panel C).
Figure 1.7 UV-Vis spectra of (A) large nanoparticles (size >5 nm), (B) medium size nanoparticles (size ~ 1.7 nm), and nanoclusters (size ~ 1.1 nm).

Whetten and co-workers studied the optical properties of a mixture of small (size ~1.1) and large (size ~ 1.7 nm) gold nanoparticle in early 2000. The large nanoparticles showed an almost featureless spectrum with a peak at ~ 1.0 eV. Surprisingly, both small and large nanoparticles showed near-Infrared (NIR) PL emission at room temperature. The PL features mainly originated from interband \(sp-sp\) transitions (Figure 1.8).

Figure 1.8 Photoluminescence spectra of small (~1.1 nm, dotted line) and large (~1.7 nm, solid line) nanoparticles excited at 1064 nm. Reprinted with permission from ref 11. Copyright 2000 American Chemical Society.
Murray’s group further focused on the optical (UV-Vis and PL) properties of Au nanoclusters along with the electrochemical features. Both techniques determined that the optical and electrochemical HOMO-LUMO gap to be 1.33 eV. The effect of the protecting ligand and charge state on photoluminescence properties of the nanoclusters (specifically \( \text{Au}_{25}(\text{SR})_{18}^z \) where \( z = 1^+, 0 \) and 1-) were further studied by the Jin group. They discovered that the higher nanocluster charge state, the greater the PL intensity.

The \( \text{Au}_{25}(\text{SR})_{18} \), the UV-Vis absorption spectrum features of the clusters vary with the charge states. This phenomenon was observed in both individually synthesized and purified samples (ex-situ) and also electrochemically generated via electrolysis (in-situ) (Figure 1.9). When varying the \( \text{Au}_{25}(\text{SR})_{18} \) charge states, the optical features such as peak positions and intensities in both UV-Vis and PL spectra change. For example, all the three charge states of \( \text{Au}_{25}(\text{SR})_{18}^z \) (\( z = 1^+, 0 \) and 1-) show a series of the similar peaks in UV-Vis spectra, while the peak intensities at 400 and 450 nm are recognized as fingerprints for each charge state. Similarly, the PL spectrum of \( \text{Au}_{25}(\text{SR})_{18}^- \) is more red-shifted than the other two. Interestingly, the peak intensity of \( \text{Au}_{25}(\text{SR})_{18}^+ \) is larger than \( \text{Au}_{25}(\text{SR})_{18}^0 \) (due to the higher probability of the electron excitation/relaxation processes). These will be addressed in this thesis.
Figure 1.9 (A) UV-Vis absorption and (B) photoluminescence spectra of Au$_{25}$(SC$_2$H$_4$Ph)$_{18}^+$. C$_6$F$_5$O$_2^-$ (black curve), Au$_{25}$(SC$_2$H$_4$Ph)$_{18}^0$ (black curve), Au$_{25}$(SC$_2$H$_4$Ph)$_{18}^-$,TOA (red curve) obtained in dichloromethane.

Wu and Jin also showed that the photoluminescence and quantum yield of Au$_{25}$ clusters can be improved by changing the protecting ligand. They concluded that the photoluminescence of the nanoclusters could be enhanced by introducing more electron rich groups in the ligand structure. They also showed that negatively charged Au$_{25}$(SG)$_{18}$ (SG= glutathione) nanoclusters revealed a stronger photoluminescence than that of the Au$_{25}$(SR)$_{18}$ (SR = 2-phenylethanol). With each synthesis of a new Au nanocluster the corresponding UV-Vis/ PL optical and redox-electrochemical properties were determined and correlated to the structure. However, to date there was not been any systematic study of the
electrogenerated chemiluminescence (ECL) of these Au nanoclusters. This thesis represents the first systematic investigation on the ECL mechanisms of a series of monodispersed prepared Au nanoclusters with various sizes and charge states ranging from Au$_{25}$(SR)$_{18}$ ($\varepsilon = 1-$, 0 and 1+), to Au$_{38}$(SR)$_{24}$ and Au$_{144}$(SR)$_{60}$.

1.2 Electrochemiluminescence or Electrogenerated Chemiluminescence (ECL)

ECL can be differentiated from both chemiluminescence (CL) and photoluminescence (PL) studies. ECL is based on the required efficient electron transfer between species electrochemically generated via oxidation and reduction reactions in the vicinity of the working electrode, resulting in the formation of an excited states(s) that eventually relaxes to the ground state with light emission (Figure 1.10, panel (I)). In an ECL process the starting species (A and B in Figure 1.10 (I)) could be the same or different. In PL a light source promotes electrons from HOMO to LUMO to generate an excited state(s) (Figure 1.10, panel (II)). Chemiluminescence (CL) happens through a reaction of two reactive species that are chemically present in a solution (Figure 1.10, panel (III)). It should be noted that both ECL and CL do not need any external light.\textsuperscript{66-67}
Figure 1.10 Schematic illustration of (I) electrochemiluminescence processes, (II) photoluminescence processes, and (III) chemiluminescence processes.

The first ECL was reported in 1964 by Hercules through the electrolysis of different aromatic hydrocarbons in organic solvents. For example, blue and red light were emitted by anthracene and rubene, respectively. The interpretation of the possible mechanism was based on the formation of radical cations and anions. An efficient electron transfer (ET) from anionic to cationic species produced an excited state. Bard’s group studied ECL of a wide range of organic and inorganic compounds, investigating their ECL processes in organic or aqueous solutions. As an analytical technique, ECL is more selective than CL. There are several advantages for ECL: (A) ECL can be produced from electroactive species, thus a non-electroactive species will not participate in a light generation process. Therefore, an ECL signal (excited state(s)) is produced through a selective process. (B) The ECL intensity can be tuned by enlarging the working electrode area. (C) Importantly, in the course of ECL the starting material does not segregate, therefore it can be used several times in the light emission.

There is a general requirement for the ECL emission based on the generation of oxidized or reduced forms. The life-time of the electrogenerated species should be long enough, so that they meet in the vicinity of the working electrode and generate emissive
excited state. The relaxation of the excited state(s) to the ground state in an ECL process is direct, meaning that there is no thermal or vibrational relaxation, while in a PL process both of these pathways can happen (Figure 1.10, panels (I) and (II)).

An ECL signal generates in two following pathways:

1.2.1 Ion annihilation route

This ECL process involves scanning or pulsing the applied potential in both cathodic and anodic regions; to produce two reactive species (R•− and R•+). The electrogenerated radical anions and cations should be stable enough to participate in an efficient electron transfer (ET), and form excited states. A typical ion annihilation process is shown in Figure 1.10, panel (I).

In addition to the life-time of the species, the ET process should be sufficient in energy to generate the excited state as shown by the following formula developed by Bard et al.:

$$-\Delta H_{ann} = E_p(R/R^•) - E_p(R/R^{+}) - 0.1 \text{ eV}$$

where $-\Delta H_{ann}$ is the enthalpy of an ion annihilation reaction between redox couples: (R/R•−) and (R/R•+). $E_p$ values are peak potentials for each redox couples; and 0.1 eV is representative of TΔS in the annihilation process. This enthalpy should be larger than the energy of the lowest excited state, Es.

1.2.2 Coreactant pathway

ECL can be enhanced by adding a coreactant that is an organic or inorganic compound easily participating in an oxidation or reduction reaction with the formation of a very reactive intermediate for further ET reactions. There are several advantages of a coreactant system: (1) A coreactant system is efficient in a small potential window, thus a strong ECL emission can be produced via this pathway; (2) Due to their high reductive or oxidative power, a low concentration can be added to the analyte solution, resulting in a significant ECL emission or enhancement; (3) The coreactant intermediates are produced...
in high concentrations. Then, they efficiently react with even unstable R− or R+ leading to an ECL emission.

Bard and co-workers introduced oxalate (C$_2$O$_4^{2-}$) as the first co-reactant in ECL process using different aromatics in organic solvents.\textsuperscript{71} The electrochemical oxidation of (C$_2$O$_4^{2-}$) produces CO$_2$ with high reduction power (E° = -1.7 eV vs. NHE). Then, the same co-reactant was used in the presence of Ru(bpy)$_3^{2+}$ in an aqueous system.\textsuperscript{72} Persulfate is an efficient co-reactant system, which is used in an acetonitrile: water mixture in the presence of Ru(bpy)$_3^{2+}$.\textsuperscript{73}

\[
S_2O_8^{2-} + e \rightarrow S_2O_8^{3-} \quad \text{(1.2)}
\]
\[
Ru(bpy)_3^{2+} + e \rightarrow Ru(bpy)_3^+ \quad \text{(1.3)}
\]
\[
Ru(bpy)_3^+ + S_2O_8^{2-} \rightarrow Ru(bpy)_3^{2+} + S_2O_8^{3-} \quad \text{(1.4)}
\]
\[
S_2O_8^{3-} \rightarrow SO_4^{-} + SO_4^{2-} \quad \text{(1.5)}
\]
\[
Ru(bpy)_3^{2+} + SO_4^{-} \rightarrow Ru(bpy)_3^{3+} + SO_4^{2-} \quad \text{(1.6)}
\]
\[
Ru(bpy)_3^{2+} + SO_4^{-} \rightarrow Ru(bpy)_3^{3+} + SO_4^{2-} \quad \text{(1.7)}
\]
\[
Ru(bpy)_3^{3+} + Ru(bpy)_3^+ \rightarrow Ru(bpy)_3^{2+} + Ru(bpy)_3^{2+} \quad \text{(1.8)}
\]

The persulfate reduction produces SO$_4^{2-}$ with very high reduction power (E° $\geq$ 3.15 eV vs. SCE).\textsuperscript{73} At close potential Ru(bpy)$_3^{2+}$ is reduced to Ru(bpy)$_3^+$ (eq. 1.3), which then participates in an electron reduction reaction with highly reactive intermediate, SO$_4^{2-}$ (eq. 1.6). The formed excited state Ru(bpy)$_3^{2+}$ relaxes to the ground state and emits light.

Recently, many different coreactants have been used. Amines and benzoyl peroxide, in particular, were discovered to have high ECL efficiency.\textsuperscript{75} Tri-$n$-propylamine (TPrA) is a tertiary amine that can be oxidized electrochemically to TPrA$^{+}$ at a potential of $\sim$ 0.81 V vs. SCE (eq. 1.8) producing a reactive radical intermediate TPrA$^+$ upon deprotonation (1.9).\textsuperscript{75} Importantly, TPrA shows a good solubility in both organic and aqueous media, making it a very good co-reactant candidate to facilitate ECL generation (A represents as an understudying compound).\textsuperscript{67}
The formed TPrA is a strong reducing agent with $E^\circ = -1.7$ eV vs. SCE, which can inject an electron to the LUMO orbital(s) of an analyte (eq. 1.10). Miao et al. investigated the classic TPrA/Ru(bpy)$_3^{2+}$ co-reactant system and summarized several mechanisms at which TPrA$^+$ and TPrA$^-$ can both participate in ECL generation process of Ru(bpy)$_3^{2+}$.\textsuperscript{77}

The ECL mechanism(s) have been investigated using different techniques such as ECL-voltage curve. In an ECL-voltage curve the ECL emitted photocurrent is recorded by using a photomultiplier tube and measured as a function of the applied potential. The obtained information is used to estimate the onset potential, where photocurrent is detected.

Recently, we established the ECL spooling technique, which enabled us to record ECL emissions in the course of the scanning potential. The spectra intervals depend on the potential scan rate, the lower the scan rate the more spectra will be obtained in the course of a potential window. More details on these techniques will be shown and discussed in the following chapters.

### 1.3 Thesis objectives

Various gold nanoclusters (AuNCs) with different compositions and structures have been synthesized. Due to their inherent optical and electrochemical features specifically their NIR emissions; it is a great opportunity to study the CL of these AuNCs in a systematic manner. Insights into their ECL emission mechanisms and their applications are anticipated. Furthermore, it is very important to further develop the \textit{in-situ} spectrophotoelectrochemistry tools such as spooling ECL spectroscopy and spooling PL spectroscopy that are not available yet and urgently needed for the innovative research. These techniques will provide an extraordinary road map for ECL controllability in intensity and wavelengths.
This thesis aims to address the above aspects by investigating the ECL of a series of AuNCs with different sizes and charge states. Chapter 2 will describe the ECL of the large nanoclusters \( \text{Au}_{144}(\text{SC}_2\text{H}_4\text{Ph})_{60} \) (with size \( \sim 1.8 \) nm) in the presence of TPrA. \( \text{Au}_{144}(\text{SC}_2\text{H}_4\text{Ph})_{60} \) can be classified between quantum dots (QDs) and nanoparticles.

Chapter 3 will depict the ECL mechanisms and efficiencies of rod shape core-shell \( \text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24} \) clusters in both annihilation and coreactants pathways by means of spooling ECL and PL spectra.

Chapters 4-6 will present our discoveries on the ECL mechanisms of the various charged \( \text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}^z \) \( (z=1-, \ 1+ \text{ and } 0) \) nanoclusters in their TPrA and BPO coreactant systems using spooling ECL spectroscopy; and thermodynamic origins of their ECL by means of the constructed Latimer diagram.

1.4 References

2) M. Faraday, Philosophical Transactions of the Royal Society of London 1857, 147, 145.


Chapter 2

2 Electrogenerated Chemiluminescence of Monodispersed \( \text{Au}_{144}(\text{SC}_2\text{H}_4\text{Ph})_{60} \) Clusters

- This Chapter has been published as a full paper. The corresponding reference is: Mahdi Hesari, Zhifeng Ding and Mark S. Workentin, *Organometallics*, **2014**, DOI: 10.1021/om500112j.

- All of the schemes, figures, and text in Chapter 2 reprinted with permission from *Organometallics*, **2014**, DOI: 10.1021/om500112j. Copyright 2014 American Chemical Society.
2.1 Introduction

Noble metal protected clusters (MPCs), such as those made of Au, in the size regime of 1.8-2 nm can be categorized at the edge of molecule-like clusters (with a size of ~1.1 nm) and quantum dots (QDs, in the range of 2.5-5 nm). From a structural point of view, the MPCs can be considered as a class of organometallic compounds because of their bonding nature originating from the metal cluster core and the organic capping ligands. Properties of semiconductor QDs have been found in the MPCs as well. The electrochemistry investigations of the gold MPCs in this size regime pioneered by different groups have revealed their capability as a quantized double-layer capacitor. However, report on their optoelectronic properties has not been as fully explored.

Among the Au MPCs, the size range of 1.8 nm and construction of Au$_{144}$(SR)$_{60}$ (where SR is 2-phenylethananethiolate and herein refereed to simply as Au$_{144}$), were investigated by scanning/transmission electron microscopy while the actual crystal structure remained unclear. Theoretically, it has been shown that the Au$_{144}$ is constructed by Au$_{114}$ polyhedral metallic core covered by 30 -SR-Au-SR- moieties on the surface. Interestingly, the electrochemical properties of Au$_{147}$, a cluster very close to Au$_{144}$ showed unique features, with at least 15 redox couples. The energy difference between Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) has been estimated to be 0.4 eV through the spectroscopic and electrochemical studies. The photochemical properties of these MPCs have been also investigated by different groups. Whetten and co-workers showed that Au MPCs with the size of 1.7 nm are photoluminescent in the near-infrared (NIR) region with a quantum yield of 4.4±1.5×10$^{-5}$. The emission has been assigned as $sp$ to $sp$-like transition.

Bard and his co-workers utilized electrogenerated chemiluminescence (ECL) to study semiconductor QDs for potential optoelectronic applications. Afterwards, QDs have been found to be a powerful ECL probe. In a typical ECL process electroactive species including radical cations and radical anions are generated in the vicinity of a biased electrode, where they meet, react via electron transfer and eventually produce an excited state to emit light. Less well studied is ECL from Au nanoparticles/clusters; we have recently shown that Au$_{25}$(SR)$_{18}^+$ is a NIR electrochemiluminescence (ECL)
emitter. Given the richer and accessible redox states of Au144, in this study we investigate this size of Au MPC as a NIR ECL emitter.

Of course, preparing a pure sample through a monodispersed synthesis protocol is a very important step in organometallic physical chemistry. Traditionally, the two-phase method (known as the Brust-Schiffrin synthesis) has been used widely to make Au140(SR)53 MPCs, leading to a mixture of Au140(SR)53 and Au38(SR)24. Thanks to advanced analyses such as matrix-assisted laser desorption ionization (MALDI) spectrometry and X-ray crystallography, exact elemental combinations have been found for Au144(SR)60 and Au25(SR)18, respectively. Au144 MPCs were prepared as the major product and Au25(SR)18 as a minor product using a Brust-Schiffrin synthetic approach. Interestingly, a one-pot protocol has now been reported, which improved the monodispersity of Au144 as the final product. Jin and his co-workers, reported that the purity and monodispersity of different MPCs/clusters such as Au144(SR)60 and Au25(SR)18 are affected by solvents used in the synthesis. They revealed that the formation of Au25(SR)18 is more favorable in THF, acetone and ethyl acetate, while Au144(SR)60 can be produced with higher yield in acetonitrile and methanol, from which there is a minor Au25(SR)18 product as well. Their proposed mechanisms were based on Au(I)SR intermediate formation, which eventually affected the size of the final products. There are also effects of gold to thiol ratio: the higher the ratio, the more monodispersed is the product.

In this chapter, we show that increasing the gold to the thiol (2-phenylethanethiol) ratio (Au:S) from 1:5 to 1:6 and 20 minute stirring at the aging step (see synthesis protocol) lead to the monodispersed Au144. The monodispersed Au144 clusters were further examined by electrochemistry and optical spectroscopy to establish structure and purity, and for the first time ECL spectroscopy. ECL of the Au144 was interrogated in both annihilation and co-reactant routes, in the absence and presence of tri-n-propylamine (TPrA), respectively. The obtained ECL spectrum of the Au144 with 50 mM TPrA showed a broad emission at a peak wavelength of 930 nm. The ECL mechanisms were further elucidated by means of electrochemistry, ECL spectroscopy and spooling photoluminescence spectroscopy performed during electrolysis of the Au144.
2.2 Experimental

2.2.1 Chemicals

Tetrachloroaurate trihydrate, tetra-\textit{n}-octylammonium bromide, acetonitrile, 2-phenylethane thiol, sodium borohydride, tri-\textit{n}-propyl amine, benzyol peroxide, dry acetonitrile, dry benzene, tera-\textit{n}-butylammonium perchlorate and Deuterated dichloromethane were purchased from Aldrich. Ethanol (95\%) was obtained from Commercial Alcohol Inc.

2.2.2 Instrumentation

UV-visible spectra were recorded using a Varian Cary 100 spectrophotometer. $^1$HNMR spectroscopy was carried out on an Inova 400 spectrometer ($^1$H: 400 MHz) in CD$_2$Cl$_2$. ESI mass spectrum measured using a Bruker mirOTOF mass spectrometer. The sample was dissolved in dichloromethane and injected to the instrument capillary. Transmission electron microscopy (TEM) images were recorded from a TEM Philips CM10.

2.2.3 Synthesis of monodispersed Au$_{144}$(SC$_2$H$_4$Ph)$_{60}$ clusters

In our preparation protocol the recent monodispersed approach was adapted with some modifications, leading to monodispersed Au$_{144}$(SR)$_{60}$.$^{32}$ Briefly, hydrogen tetrachloroaurate (2.54 mmol) and tetra-\textit{n}-octylammonium bromide (TOABr) (3.05 mmol) were dissolved in acetonitrile at room temperature. The mixture was stirred for 10 minutes, while cooling to 0 °C. 2-Phenylethanethiol, (6 eq., relative to Au), was added to the cooled mixture and stirred until white-opaque mixture formed. At this point, 10 eq. ice-cold sodium borohydride aqueous solution was poured to the flask all at once and stirring speed was increased. The gold clusters formed rapidly. After 20 minutes (aging step) the reaction product was gravity filtered and washed with methanol-water mixture and finally with methanol to remove excess of thiol and sodium borohydride resulting in a black solid. The black solid was washed first with acetonitrile to remove possibly formed Au$_{25}$(SR)$_{18}$ clusters. The acetonitrile solution obtained during the wash was
examined with UV-Vis spectroscopy and no Au$_{25}$(SR)$_{18}$ traces in the spectrum were found. Giving further aging time did not affect the purity or yield (24% based on Au) of the final product. Electrospray ionization (ESI) mass spectrometry, $^1$H NMR spectroscopy, UV-Vis spectroscopy and transmission electron microscopy (TEM) were used to examine the purity of the product. The UV-Vis spectrum showed the expected features, including the shoulder at 520 nm (Figure 2.1) and no evidence of any Au$_{25}$ impurities.

![UV-Vis spectrum of Au$_{144}$(SC$_2$H$_4$Ph)$_{60}$ in CH$_2$Cl$_2$.](image)

**Figure 2.1** UV-Vis spectrum of Au$_{144}$(SC$_2$H$_4$Ph)$_{60}$ in CH$_2$Cl$_2$.

The molecular mass value of the Au$_{144}$(SC$_2$H$_4$Ph)$_{60}$ cluster is 36596.5059 Da, and ESI mass spectrum show two main peaks at 12198.8353 Da (A) and 9149.1261 Da (B) corresponding to the 3$^+$ and 4$^+$ molecular ions mass of the Au$_{144}$ cluster (Figure 2.2).
Figure 2.2 Electrospary ionization (ESI) mass spectrum of Au\textsubscript{144}(SC\textsubscript{2}H\textsubscript{4}Ph)\textsubscript{60}. Peaks (A) and (B) show 3+ and 4+ molecular ion fragments. The insets show single peak for each fragments.

Also, transmission electron microscopy (TEM) image analysis showed the expected cluster size in 1.8 nm regime (Figure 2.3).
As expected proton nuclear magnetic resonance ($^1$H NMR) spectroscopy confirmed that there is no tetra-$n$-octylammonium counter ion in the molecular structure (Figure 2.4), and thus Au$_{144}$ has a zero charge. The broadness of the proton spectrum could be an indication of different chemical environments for the ligand on the nanoparticles surface.
Figure 2.4 $^1$H NMR spectrum of Au$_{144}$(SC$_2$H$_4$Ph)$_{60}$ recorded in CD$_2$Cl$_2$. The asterisk indicates the solvent residual. Peaks at 2-4 ppm and ~7 ppm are corresponding methylene and aromatic protons in the phenylethene thiolate ligands, respectively. The asterisk shows the residual solvent peak.

2.2.4 General procedures for electrochemistry and electrogenerated chemiluminescence of Au$_{144}$(SC$_2$H$_4$Ph)$_{60}$

The working electrode was a 2 mm diameter Pt disc in-laid in a glass sheath as the working electrode (WE), a coiled Pt wire as the counter electrode (CE), and a coiled Pt wire as the quasi reference electrode (QRE). An Ag wire used as the QRE was found to react with the Au clusters during electrochemistry processes and so was not used. After each experiment, the electrochemical potential window was calibrated using ferrocene (Fc) as the internal standard. The redox potential of the ferrocenium/ferrocene (Fc$^+/$/Fc) couple was taken as 0.424 V vs. SCE.$^{33}$ For annihilation ECL studies, Au$_{144}$(SC$_2$H$_4$Ph)$_{60}$ clusters was added to a specialized electrochemical cell with a flat Pyrex window at the bottom for ECL detection. To this cell was added 0.1 M TBAP (tetra-$n$-butylammonium perchlorate) as the supporting electrolyte in 1:1 anhydrous acetonitrile (1.5 mL) :
The cell was assembled in a glove box. For the coreactant ECL experiments, 50 mM TPrA (tri-\textit{n}-propylamine) was added to the above solution and assembled under an Ar (99.999\%) stream.

The cyclic and differential pulse voltammetry were conducted on a CHI 610A electrochemical analyzer (CH Instruments, Austin, TX). The experimental parameters for the cyclic voltammograms (CVs) are listed here: 0.000 V initial potential in experimental scale, positive or negative initial scan polarity, 0.1 Vs\(^{-1}\) as the scan rate, 4 sweep segments, 0.001 V sample interval, and 2 s of quiet time. The DPVs were obtained at peak amplitude of 0.05 V, a pulse width of 0.05 s, 2 mV increment per cycle, and a pulse period of 0.2 s, and 2 s of quiet time.

The ECL-voltage curves were obtained using the CHI 610A coupled with a photomultiplier tube (PMT, R928, Hamamatsu, Japan) held at -750 V with a high voltage power supply. The ECL collected by the PMT under the flat Pyrex window at the bottom of the cell was measured as a photocurrent, and transformed to a voltage signal, using a picoammeter/voltage source (Keithley 6487, Cleveland, OH). The potential, current signals from the electrochemical workstation, and the photocurrent signal from the picoammeter were sent simultaneously through a DAQ board (DAQ 6052E, National Instruments, Austin, TX) in a computer. The data acquisition system was controlled from a custom-made LabVIEW program (ECL_PMT610a.vi, National Instruments, Austin, TX). The photosensitivity on the picoammeter was set manually in order to avoid the saturation. The intensities \textit{versus} wavelengths (ECL spectra) were recorded by an Andor Technology program. Similar to the CV experiments, the samples were scanned between their redox potentials.

### 2.2.5 Spooling photoluminescence spectroscopy

The photoluminescence spectra of various \textit{Au}_\textit{144} charge states (Figure 2.11) were obtained in the course of electrolysis using a 1 mm thin layer quartz cell (BASi) containing the same 0.1 mM \textit{Au}_\textit{144} electrolyte solution used in the electrochemical and ECL studies, freshly prepared under Ar atmosphere. The electrolysis was performed
using a Pt mesh as the working electrode, a nonaqueous reference electrode (Ag wire immersed in 0.01 M Ag⁺ / 0.1 M TBAP in acetonitrile), and a Pt wire as the counter electrodes. The mesh electrode area was excited using a 532 nm laser, and spooling photoluminescence spectra were acquired from the narrow side of the thin layer solution by means of the same CCD camera and Acton spectrograph set. A long-pass edge filter was placed between the sample and the spectrograph entrance to cut the excitation wavelength and harmonic peaks.

2.3 Results and Discussions

2.3.1 Electrochemistry of the Au₁₄₄(SC₂H₄Ph)₆₀

Figure 2.5 shows the differential pulse voltammograms (DPVs) of 0.05 mM of the monodispersed Au₁₄₄ in 1:1 benzene: acetonitrile solvent mixture containing 0.1 M tetra-n-buthylammonium perchlorate (TBAP) as the supporting electrolyte. A 2 mm Pt disk inlaid in a glass sheath was used as the working electrode and a Pt wire and mesh were served as reference and counter electrodes. All potential was calibrated against the ferrocenium/ferrocene couple, whose formal potential in acetonitrile: benzene 1:1 mixture is 0.424 V vs. saturated calomel electrode (SCE). The recorded DPVs in both oxidation and reduction directions show several redox peaks involved in the multistep electron transfer due to quantized charge transfer in the Au₁₄₄ core (Figure 2.5).
Figure 2.5 Differential pulse voltammograms (DPVs) of 0.05 mM of the Au$_{144}$ in 1:1 benzene: acetonitrile mixture, containing 0.1 M TBAP at a scan rate of 50 mVs$^{-1}$ on a Pt WE disk. Charge states have been assigned from the open circuit potential. The DPVs were obtained with a peak amplitude of 0.05 V, a pulse width of 0.05 s, an increment of 2 mV per cycle, a pulse period of 0.2 s, and a quiet time of 2 s. The arrows indicate potential scanning directions.

The DPVs demonstrate well-defined electrochemical signals in both cathodic and anodic scans, which illustrates a good reversibility. Importantly, there is no trace of Au$_{25}$ electrochemical signals (at $E_p$~ -0.08 and 0.24 V vs. SCE), which causes extra peak(s) in DPV voltammograms.$^{34}$ Anodic and cathodic peak to peak separation ($\Delta V=4$ mV) is fairly consistent over the DPVs.$^{14}$ The above observations agree well with those reported in the literature.$^{6, 14, 35}$ The results indicated fairly stable electrochemical behavior of the gold core under different electrochemical conditions. The electrochemical features of the Au$_{144}$ provides reliable evidence of the cluster purity for further use in the ECL experiments.

Figure 2.6 also shows the corresponding cyclic voltammogram (CV) of the same
solution, which reveals multiple reactions with clear features as observed in the DPV.

![Cyclic voltammogram](image)

**Figure 2.6** Cyclic voltammogram of 0.05 mM Au$_{144}$(SC$_2$H$_4$Ph)$_{60}$ in 1:1 benzene:acetonitrile containing 0.1 M TBAP, at a scan rate of 100 mV s$^{-1}$.

The open circuit potential was measured as 0.004 V vs. SCE, representing no charge on the Au$_{144}$ clusters. Thus, the redox couples can be assigned from 0/1+ to 5+/6+ and also 0/1- to 7-/8- in both oxidative and reductive directions, respectively (Figure 2.5). The loss of reversibility beyond the 6-/7- states is known to be due to the reductive desorption of the thiolate ligands at these more negative potentials.

### 2.3.2 Electrogenerated chemiluminescence study of Au$_{144}$(SC$_2$H$_4$Ph)$_{60}$

The electrogenerated chemiluminescence (ECL) of 0.05 mM of the above Au$_{144}$ cluster solution was first investigated in the annihilation mechanistic route. In a typical annihilation process the applied potential produces radical cation and anion or other charged species, which have to be sufficiently stable in order to react together. These
reactive species eventually interact through an electron transfer process and generate excited state(s). In the annihilation experiment with Au\textsubscript{144}, the applied potential was scanned between the electrochemical active potentials in a range between 1.25 and -1.6 vs. SCE (Figure 2.7).

![ECL-voltage curve](image)

**Figure 2.7** ECL-voltage curve of 0.05 mM Au\textsubscript{144}(SC\textsubscript{2}H\textsubscript{4}Ph)\textsubscript{60} in 1:1 benzene: acetonitrile containing 0.1 M TBAP during annihilation at a scan rate of 50 mVs\textsuperscript{-1}. The arrow indicates the direction of initial potential scanning.

Toward the negative and positive potential scans the respective redox states of Au\textsubscript{144} will form. The emission of the formed excited state (due to electron transfer of donor, Au\textsubscript{144}\textsuperscript{−}, and acceptor, Au\textsubscript{144}\textsuperscript{+}) was not observed. This is likely due to the small HOMO-LUMO gap with 0.186 eV (exp.) and 0.175 eV (cal.).\textsuperscript{39} It has been argued that the small HOMO-LUMO gaps for Au\textsubscript{144} clusters originated from the presence of subshells in the electronic configuration.\textsuperscript{13} While the other clusters such as Au\textsubscript{25} and Au\textsubscript{38} (with core-shell structures) show larger HOMO-LUMO gap with 1.33 and 0.9 eV\textsuperscript{40-41} and importantly resulted in stronger luminescence.

Different coreactant systems have been employed to enhance the light emission
intensity ECL process when direct annihilation yields no or low ECL.\textsuperscript{42-43} For instance, benzoyle peroxide (BPO) and tri-\textit{n}-propyl amine (TPrA) or inorganic salts such as C\textsubscript{2}O\textsubscript{4}\textsuperscript{2-} and S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}, undergo oxidation or reduction reactions to produce radicals with high reduction or oxidation power. These radicals can react with an appropriate reaction partner generated in the vicinity of the electrode \textit{via} electron transfer and generate excited state(s) to emit light.\textsuperscript{42} Tri-\textit{n}-propylamine (TPrA) has been used as a popular coreactant in ECL system due to its solubility in both organic and aqueous solutions.\textsuperscript{42} Also, TPrA is an efficient ECL mediator because it generates the TPrA radical (TPrA\textsuperscript{•}), which has a high reduction potential, in a narrow oxidation potential window. Upon oxidation of TPrA at the working electrode TPrA\textsuperscript{•+} forms, which then undergoes a fast deprotonation and produces TPrA\textsuperscript{•}. The TPrA\textsuperscript{•} (E\textsubscript{°} = -1.7 eV) can inject electrons to the LUMO orbitals of the ECL emitter(s).\textsuperscript{44} Figure 2 shows the cyclic voltammogram (CV) of 0.05 mM of Au\textsubscript{144} clusters along with photocurrent curve (ECL-voltage) in the presence of 50 mM TPrA in 1:1 acetonitrile: benzene mixture. The CV is dominated by the oxidation of TPrA which is in very high concentration relative to the [Au\textsubscript{144}].

\textbf{Figure 2.8} ECL-voltage curve of 0.05 mM Au\textsubscript{144}(SC\textsubscript{2}H\textsubscript{4}Ph)\textsubscript{60} with 50 mM TPrA in 1:1 benzene: acetonitrile mixture, containing 0.1 M TBAP, scan rate 100 mVs\textsuperscript{-1}.  

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The onset of the ECL-voltage curve was found at ca. 0.8 V vs. SCE. At this potential, Au\textsubscript{144} is oxidized to Au\textsubscript{144}\textsuperscript{5+} (see Figure 2.8) and the reducing agent TPrA\textsuperscript{*} is being generated (i.e., TPrA oxidation has begun). The reducing power of TPrA\textsuperscript{*} (E\textsuperscript{o} = -1.7 eV vs. SCE) is high enough to inject an electron to the LUMO of Au\textsubscript{144}\textsuperscript{5+} that would produce Au\textsubscript{144}\textsuperscript{4++}. The Au\textsubscript{144}\textsuperscript{4++} is likely responsible for the observed ECL emitted light in the NIR at around 930 nm (Figure 2.10). As a control the same experiment was performed on the same solution but without any added Au\textsubscript{144} over the entire potential. Importantly, no ECL light is observed in the absence of the Au\textsubscript{144} nanocluster (Figure S1).

Scheme 2.1 represents the ECL generation mechanism for the experiment demonstrated in Figure 2.8 up to a potential maximum of 0.9 V. The mechanism shows that at the higher potential regions (>0.8 V vs. SCE) where Au\textsubscript{144}\textsuperscript{5+} is generated it will react with the highly reducing TPrA\textsuperscript{*} to generate Au\textsubscript{144}\textsuperscript{4+*}, which then emits ECL. The Au\textsubscript{144}\textsuperscript{4+*} this formed can then be involved in a catalytic reaction to regenerate Au\textsubscript{144}\textsuperscript{5+} at these higher potentials.
Scheme 2.1 The proposed ECL generation mechanism of the Au$_{144}$ with 50 mM TPrA. The potential window is between -0.089 and 0.9 V vs. SCE.
To facilitate the elucidation of the source of the ECL and its mechanism we can compare this ECL spectrum to the *in-situ* photoluminescence (PL) spectra of the various oxidation states of Au$_{144}$. In these experiments we performed *in-situ* spectrophotooelectrochemistry in the same electrolyte solution. Here, a 1 mm thin layer quartz cell (BASi) was used, containing the same 0.1 mM Au$_{144}$ electrolyte solution used in the electrochemical and ECL studies. The applied potential of a thin mesh Pt working electrode was held at the appropriate values to form separately and consecutively the desired charge species: Au$_{144}^{0/1+}$, Au$_{144}^{1+/2+}$, Au$_{144}^{2+/3+}$, Au$_{144}^{3+/4+}$, Au$_{144}^{4+/5+}$, and Au$_{144}^{5+/6+}$. Meanwhile spooling PL spectra upon excitation of each of the charge states generated by the electrolysis at this electrode with a 532 nm laser of the solution were recorded to help tracking the PL emission wavelength and intensity. Figure 2.11 shows the PL spectra of different charge species Au$_{144}$(SR)$_{60}^z$ (z= 0, 1+, 2+, 3+, 4+, 5+ and 6+) (spectra 2.11 A-G). The ECL spectrum pattern shown in Figure 2.6 is very similar to the PL measured during the excitation of the *in-situ* generated of Au$_{144}^{4+}$ (Figure 2.11 E).
The so-called self-absorption process (an inner filter effect, which includes re-adsorption by the MPC in the solution) was not very evident.\textsuperscript{45}

\textbf{Figure 2.10} Photoluminescence spectra (accumulated for 10 s) of the Au\textsubscript{144}\textsuperscript{z} (A-G corresponding to z= 0, 1+, 2+, 3+, 4+, 5+ and 6+, respectively) electrogenerated in the same electrolyte as the experiment in Figure 2.5. A 532 nm laser was used for photoinduced excitation at each potential.
The Au$_{144}$/TPrA (50 mM) co-reactant system was then oxidized to the upper limit potential of 1.20 V, at which potential Au$_{144}^{6+}$ is formed. Au$_{144}^{6+}$ can also participate in an electron transfer with the electrogenerated TPrA radical in the vicinity of the working electrode. Scheme 2 shows the proposed mechanism for extended potential window (-0.089 to 1.20 V vs. SCE).

Scheme 2.2 The proposed ECL emission mechanism of Au$_{144}$(SC$_2$H$_4$Ph)$_{60}$ with 50 mM TPrA. The potential window is -0.089 to 1.2 V vs. SCE.

The accumulated ECL spectrum measured under these conditions also showed a peak at around 930 nm (Figure 2.8). The Au$_{144}^{6+}$/TPrA$^*$ participates in an electron transfer reaction, where TPrA$^*$ injected an electron to the LUMO orbitals of Au$_{144}^{6+}$. As a
result, $\text{Au}_{144}^{5+\star}$ was generated, which then relaxed to the ground state and emitted light. Interestingly, it can be seen that the recorded ECL spectrum (Figure 2.8) showed a higher emission count, (twice as intense) relative to the ECL spectrum obtained at the lower potential limit (Figure 2.6). At this higher potential, a higher [TPrA$^\cdot$] is generated, which leads to increased reactivity, a higher $\text{Au}_{144}^{5+\star}$ concentration and greater intensity.

Scheme 2.2 represents the ECL mechanism corresponding to $\text{Au}_{144}^{6+}$/TPrA system, where $\text{Au}_{144}^{5+\star}$ can be formed via electron transfer between $\text{Au}_{144}^{6+}$ and TPrA$^\cdot$. The corresponding excited state returns to the ground state and generates $\text{Au}_{144}^{5+}$, which can participate in an oxidation process and re-generates $\text{Au}_{144}^{6+}$ in a catalytic route. Again the ECL spectrum (Figure 2.11) matched the PL spectrum of $\text{Au}_{144}^{5+}$ (Figure 2.10 F), suggesting the ECL emission is from the excited state, $\text{Au}_{144}^{5+\star}$.

![Figure 2.11](image)  

Figure 2.11 ECL spectrum of the $\text{Au}_{144}$/TPrA coreactant system recorded during potential scanning between -0.089 and 1.2 V vs. SCE.

2.4 Conclusion

In summary, $\text{Au}_{144}$ was synthesized within 20 mins using a modified one-pot
protocol with high purity and monodispersity. Importantly, no ECL light was observed either in the course of annihilation (in the absence of TPrA) or just of the TPrA oxidation, providing a clear evidence for ECL generation via the co-reactant route. NIR ECL of the Au$_{144}$ clusters in the presence of 50 mM TPrA was observed for the first time. The electrogenerated TPrA$^-$ has reducing power of -$1.7$ eV, injecting an electron to Au$_{144}^{5+}$ and Au$_{144}^{6+}$ LUMOs resulting in the generation of Au$_{144}^{4+*}$ and Au$_{144}^{5+*}$, respectively. These two excited states relaxed to the ground state and emitted NIR light with a peak wavelength of 930 nm. The ECL intensity from the Au$_{144}$/TPrA system is relatively weak due to the short lifetime of the electrogenerated Au$_{144}^{n+}$ species, its reactivity or the small HOMO-LUMO gap (with 0.186 eV). Importantly, the NIR emission is very good for live cell and tissue imaging, because it is not absorbed. Thus, although relatively weak the ECL observed for the stable Au$_{144}$ gold cluster may find applications for in vivo bio-imaging.$^{46}$

2.5 References


Chapter 3

3 Highly Efficient Electrogendenerated Chemiluminescence of \( \text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24} \) Nanoclusters

• This Chapter has been submitted as a full paper. The corresponding reference is: Mahdi Hesari, Mark S. Workentin, and Zhifeng Ding, ACS Nano, 2014, 8, 8543-8553.

• All of the schemes, figures, and text in Chapter 2 reprinted with permission from ACS Nano, 2014, 8, 8543-8553. Copyright 2014 American Chemical Society.
3.1 Introduction

The distinct molecular-like properties of thiol-protected gold nanoclusters with \( \text{Au}_n(\text{SR})_m \) (\( n < 100 \), SR represents a thiol ligand) and their corresponding extraordinary optical,\(^1\)\(^-\)\(^6\) electrochemical,\(^7\)\(^-\)\(^9\) and catalytic\(^10\)\(^-\)\(^13\) properties, have made them the focus of a wide range of fundamental and practical studies.\(^6\)\(^,\)\(^14\) Included among these studies are extensive efforts to synthesize and characterize novel Au core sizes and adjust the functionality of the protecting ligands, as a means to probe the various factors that alter the cluster properties.\(^15\)\(^-\)\(^18\) Knowledge of the discrete optical and electrochemical characteristics permit investigations that explore the mechanisms of electrogenerated chemiluminescence or electrochemiluminescence (ECL) of these Au nanoclusters. ECL is a photoelectrochemical process, in which electrogenerated reactive species, radical cations or anions or other charged redox states of Au nanoclusters specifically here, participate in an electron transfer (ET) to produce excited states, which emit light upon relaxing to ground states.\(^19\)\(^-\)\(^20\) The ECL light emission wavelength depends on the energy gap between the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbitals (LUMO). ECL signals, that do not require a laser light source,\(^21\) have been used for a wide range of electroanalytical detections mainly due to its high signal to noise (background) ratio.\(^22\)\(^-\)\(^23\) The ECL emission can be generated and controlled via a working electrode potential, in order to trigger a specific detection in a mixture of analytes.\(^24\)

We have recently reported the near infrared (NIR) ECL observed from \( \text{Au}_{25}(\text{SR})_{18}^+ \) in both annihilation and coreactant routes.\(^20\) These ECL peak wavelengths were found to be in the NIR region, which correlated with the clusters’ HOMO-LUMO energy gaps. Furthermore, we employed our newly established spooling ECL spectroscopy to gain insight into the mechanism of the ECL process. In the spooling technique, ECL spectra are recorded in the course of the applied potential scanning. Any changes in the emission peak wavelength can be tracked to correlate to the corresponding potentials. The observed NIR emission for \( \text{Au}_{25}(\text{SR})_{18}^+ \) opens up not only opportunities for it to be utilized in bioanalytical applications (because of the wavelength) but also set
the stage to extend the mechanistic study to other charged Au$_{25}$(SR)$_{18}$ ($\varepsilon = -1, 0$) nanoclusters and various sized Au nanoclusters. These studies will provide insight into the effects of the Au cluster core size, its charges and the protecting ligands on the ECL wavelength, intensity and efficiency.

Herein, we report ECL of the very interesting Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ (Au$_{38}$, SC$_2$H$_4$Ph= 2-phenylethanethiol) nanocluster, in which the face-fused biicosahedral Au$_{23}$ core differentiates from other studied clusters in that two Au$_{13}$ icosahedra fused together via sharing a common Au$_3$ face$^{25}$. The atomic structure of this nanocluster results in a HOMO-LUMO gap of 0.9 eV$^{8,9}$ and it exhibits an extremely well-defined electrochemical behavior. This will allow a thorough interrogation of the ECL mechanism in the presence of coreactants. It was discovered that coreactants such as tri-$n$-propylamine (TPrA) and benzoyl peroxide (BPO) enhanced greatly the ECL emission of Au$_{38}$ clusters while that in the annihilation route was very weak. In the two coreactant reactant systems, either the high reducing power of the electrogenerated TPrA$^-$ ($E^\circ = -1.7$ eV)$^{26}$ or high oxidizing power of the benzoate radical (C$_6$H$_5$CO$_2$)$^-$ ($E^\circ = +1.5$ eV)$^{27}$ reacts with the various defined redox states of the Au$_{38}$ generated in the anodic (for TPrA) or cathodic (for BPO) potential ranges, respectively. The resulting ECL spectra revealed a peak wavelength at ca. 930 nm in the presence of either TPrA or BPO as coreactants. The combination of ECL-voltage curves with spooling ECL spectra explicitly elucidated ECL mechanisms, where Au$_{38}^{+*}$, Au$_{38}^{2+*}$ and Au$_{38}^{-*}$ were the electrogenerated excited species emitting light. In the Au$_{38}$/TPrA coreactant system, the TPrA$^-$ reacted with Au$_{38}^{2+}$ and Au$_{38}^{4+}$ electrogenerated in the anodic region, producing Au$_{38}^{+*}$ and Au$_{38}^{3+*}$. In the cathodic region, the benzoate radical and Au$_{38}^{2-}$ were formed in the Au$_{38}$/BPO system to produce Au$_{38}^{-*}$. All these three excited species emitted at the same peak wavelength. This was verified through a careful in situ spectrophotocatalytic study of these Au$_{38}$(SR)$_{24}^z$ species ($z=2^-, 1^-, 0^+, 1^+,$ 2$^+$ and 3$^+/4^+$) generated independently via electrolysis, at various applied potentials. The observation of this very strong NIR ECL, and the similarities of the emission for each of the corresponding excited states allow control of the ECL intensity in the NIR region that is amenable for future bioanalytical applications.
3.2 Experimental

3.2.1 Chemicals

Hydrogen tetrachloroaurate trihydrate (Aldrich, 99.9%), phenylethanolthiol (Aldrich, 98%), sodium borohydride (Aldrich, 99%), methanol (Caledon, 99.8%), trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, Aldrich 98%), ethanol (Caledon, 99.8%), and acetonitrile (Caledon) were used as received. Tetra-n-butylammonium perchlorate was provided by Fluka (99 %) and kept in dedicator before use. Anhydrous acetonitrile (99.8 %) and anhydrous benzene (99.8 %), benzoyl peroxide (Luperox® A98, 98 %), Tri-n-propylamine (Aldrich, 98%) were purchased from Aldrich.

3.2.2 Synthesis of Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ clusters

Monodispersed Au$_{38}$ clusters were prepared according to size selecting synthetic procedure with some modification. Briefly, 196.6 mg (0.5 mmol) HAuCl$_4$·3H$_2$O and 614.0 mg (2.0 mmol) glutathione powder were mixed in 20 mL of acetone at room temperature, which was stirred for 20 min. The resulted yellowish cloudy suspension was then cooled to 0 °C and kept for another 20 min. A solution of NaBH$_4$ (5 mmol, 189.0 mg, dissolved in 6 mL of cold deionized water) was rapidly added to the suspension under vigorous stirring. The color of the solution immediately turned black after the addition, indicating the formation of clusters. The black Au$_n$(SG)$_m$ intermediate clusters were found to precipitate out and stick to the inner wall of the flask. The supernatant was then decanted and the residual was dried. The obtained Au$_n$(SG)$_m$ was redispersed in 6 mL of nanopure water, to which a mixture of 0.6 mL of ethanol, 2 mL of toluene, and 2.5 mL of phenylethenethiol was added. The biphasic solution was heated to and maintained at 80 °C under reflux for overnight. It has been observed that by following the previously reported procedure by Qian’s protocol a metallic layer of gold is formed on the reaction flask after 40 hours reflux. This is an indication of decomposition of the desired product, when the protecting ligand removes from the gold clusters under the
thermal condition. Thus, we increased phenyethene thiol ratio slightly higher (2.5 mL), while shorter reaction time (18 hours at 80 °C) to prevent the desired product decomposition. Our modification led to the formation of desired Au_{38} clusters overnight with ~ 30% yield based on elemental Au. The UV-Vis spectrum of the crude product was measured after 18 hours and compared to the reported spectrum. Then, the reaction was cooled down and the mixture was extracted for several times with toluene and the organic phase was extracted using dichloromethane and collected. The toluene was evaporated under vacuum, and a dark green crude oily product formed. The solid was obtained after washing the oily crude product thoroughly with methanol to remove excess of the thiol. The pure Au_{38}(SC_2H_4Ph)_24 clusters were extracted using dichloromethane and characterized by UV-Vis-NIR.

3.2.3 Characterization

UV-visible-NIR spectra were recorded using a Varian Cary 5000 spectrophotometer. The UV-Vis-NIR spectrum of the pure compound showing distinct features of Au_{38} clusters with peak wavelength at 478 (2.60 eV), 626 (1.98 eV), 743 (1.66) and 1028 (1.20 eV) nm (Figure 3.1). The MALDI spectrum showed a parent peak at 10776.0 Da (Cal. 10778.0 Da) and other peaks produced after removal of Au_4(SR)_4 fragments (Figure 3.2).
**Figure 3.1** UV-Vis-NIR absorption spectrum of 0.05 mM of the Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ in 1:1 acetonitrile: benzene mixture in wavelength (left) and in energy, eV, (right) scales, which is in agreement with those from the DFT calculations.$^1$

An AB Applied Biosystem mass spectrometer (4700 Proteomics Analyzer) was employed to obtain the MALDI-TOF spectra (Figure 3.2). The sample was prepared by mixing 0.2:1000 analyte to matrix ratio. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) is used as the matrix. Then, 7 µL of the mixture was casted on the target plate and air-dried.
3.2.4 Electrochemistry and ECL instrumentations

The electrochemistry and ECL of the Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ cluster were carried out using a 2 mm diameter Pt disc inlaid in a glass sheath as the working electrode (WE), a coiled Pt wire as the counter electrode (CE), and a coiled Pt wire as the quasi reference electrode (QRE). After each experiment, the electrochemical potential window was calibrated using ferrocene as the internal standard. The redox potential of the ferrocene/ferrocenium (Fc/Fc$^+$) couple was taken as 0.424 V vs. SCE.$^{28}$ In annihilation ECL studies, a solution containing approximately 3 mg of Au$_{38}$ clusters, 0.1 M TBAP as the supporting electrolyte and 1.5 mL anhydrous acetonitrile and anhydrous benzene was added to the electrochemical cell with a flat Pyrex window at the bottom for detection of generated ECL, which was assembled in a glove box. For coreactant studies, 5.0×10$^{-3}$ M BPO was added to the annihilation solution and the air-tighten cell was also assembled in

Figure 3.2 Matrix-assistance laser desorption ionization spectrum of the Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$. 
a dry box. Different concentrations of TPrA were also added to the electrochemical cell under Ar (99.999%) blanket to prevent oxygen entering the sample solution.

The cyclic voltammetry were performed on a CHI 610A electrochemical analyzer (CH Instruments, Austin, TX). The general experimental parameters for cyclic voltammograms (CVs) are listed here: 0.000 V initial potential in experimental scale, positive or negative initial scan polarity, 0.1 V s⁻¹ scan rate, 4 sweep segments, 0.001 V sample interval, 2 s quiet time, 1.5×10⁻⁵ AV⁻¹ sensitivity. The ECL-voltage curves were obtained using the CHI 610A coupled with a photomultiplier tube (PMT, R928, Hamamatsu, Japan) held at -750 V with a high voltage power supply. The ECL was collected by the PMT under the flat Pyrex window at the bottom of the cell was measured as a photocurrent, and transformed to a voltage signal, using a picoammeter/voltage source (Keithley 6487, Cleveland, OH). The potential, current signals from the electrochemical workstation, and the photocurrent signal from the picoammeter were sent simultaneously through a DAQ board (DAQ 6052E, National Instruments, Austin, TX) to a computer. The data acquisition system was controlled from a custom-made LabVIEW program (ECL_PMT610a.vi, National Instruments, Austin, TX). The photosensitivity on the picoammeter was set manually in order to avoid the saturation.

The ECL spectra were recorded using the Andor Technology program. Similar to the CV experiments, the samples were scanned between their redox potentials. Since the ECL is in NIR region, ECL spectroscopy was conducted on an Acton 2300i spectrograph with two gratings (50 l/mm blazed at 600 nm and 300 l/mm blazed at 700 nm) and an Andor iDUS CCD camera (Model DU401-BR-DD-352). The set of the spectrograph and camera was calibrated using a mercury lamp each time. The accumulation spectra were recorded during two successive potential scan cycles as discussed in each experiment. The spooling ECL spectra were acquired at a time interval of 1 s or a potential increment of 100 mV with the potential scan rate of 100 mVs⁻¹.

In-situ spectrophotoelectrochemistry. The photoluminescence spectra of various Au₃₈ charge states (Figure 3.10) were obtained in the course of electrolysis using 1 mm thin layer quartz cell (BASi) containing the same 0.1 mM Au₃₈ electrolyte solution used
in the electrochemical and ECL studies, freshly prepared under Ar atmosphere. The electrolysis was performed using a Pt mesh as the working electrode, a nonaqueous reference electrode (Ag wire immersed in 0.01 M Ag⁺ / 0.1 M TBAP in acetonitrile), and a Pt wire as the counter electrodes. The mesh electrode area was excited using a 532 nm laser, and single or spooling photoluminescence spectra were acquired from the narrow side of the thin layer solution by means of the same CCD camera and Acton spectrograph set. A long-pass edge filter was placed between the sample and the spectrograph entrance to cut the excitation wavelength and harmonic peaks.

3.3 Results and discussion

3.3.1 Correlating electrochemistry of the Au₃₈ to its electronic configuration

Figure 3.3 shows the cyclic voltammogram of 0.1 mM Au₃₈ in 1:1 acetonitrile:benzene mixture containing 0.1 M tetra-n-butylammonium perchlorate (TBAP) as the supporting electrolyte. The Au₃₈ undergoes five successive redox reactions in both anodic and cathodic regions with formal potentials of -0.762, -1.010, 0.390, 0.598 and 0.994 V vs. SCE, assigned as Red₁ (Au₃₈⁺/Au₃₈⁻) and Red₂ (Au₃₈⁻/Au₃₈²⁻), Ox₁ (Au₃₈⁺/Au₃₈₀), Ox₂ (Au₃₈²⁺/Au₃₈⁺), and Ox₃ (Au₃₈³⁺/Au₃₈²⁺), respectively. The above redox reaction pattern agrees well with that reported by Quinn and Liljeroth et al. for their pure Au₃₈ prepared using a different method.⁸
Figure 3.3 Cyclic voltammogram (purple) and ECL-voltage curve (red) of 0.1 mM Au$_{38}$ nanoclusters in 1:1 acetonitrile: benzene mixture containing 0.1 M TBAP, which was recorded in a potential window between -1.28 and 1.22 V vs. SCE at a scan rate of 100 mVs$^{-1}$. The arrow indicates the direction of the potential scanning. The insets indicate the electronic configurations of various redox states.

Aiken, Häkinnen, Tsukuda and co-workers used experimental powder XRD data and employed DFT calculations$^{29}$ to predict along with the Zeng group$^{30}$ the structure of the Au$_{38}$ as Au$_{23}@(Au(SR)_2)_3(Au_2(SR)_3)_6$ having a nanorode-like biicosahedral core plus three monomeric staples (RS-Au-SR) and six dimeric staples (RS-Au-S(R)-Au-SR). This prediction was later verified by the Jin group, who successfully isolated and refined the Au$_{38}$ single crystal structure.$^{25}$ The calculations of the Au$_{38}$ electronic structure$^{29}$ revealed that the Au$_{38}$ has two degenerated HOMOs occupied with four electrons, and two degenerated LUMOs. This information provided the basis of the assignments for the electrochemical features shown in Figure 3.3. In the anodic scan, the Au$_{38}$ undergoes two
successive reversible one-electron oxidation reactions, as illustrated by the insets for HOMO-LUMO configurations in Figure 3.3. Assuming the original energies of the two degenerated HOMOs are maintained upon oxidation, the difference between the formal potentials of the Ox$_1$ and Ox$_2$ (0.208 V) is likely the result of less static repulsion and in turn greater driving force needed to remove the second electron after the first oxidation. The Au$_{38}^{2+}$ was further oxidized (Ox$_3$) irreversibly when the applied potential moved to more positive potentials. From the ratio of the Ox$_3$ peak current to that of Ox$_2$, it appears that the next two electrons in the degenerate HOMOs are removed at the same or very similar potential and appear as a single two electron wave (Ox$_3$ reaction). When the scan rate was increased to 1000 mVs$^{-1}$, it is evident that the first two of the oxidation reactions are reversible (Figure 3.4).

**Figure 3.4** Cyclic voltammograms (CVs) of the 0.1 mM Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ in 1:1 acetonitrile: benzene mixture containing 0.1 M TBAP at scan rates of 100 (red) and 1000 (black) mVs$^{-1}$. 

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To further test the reversibility of the Ox₁ and Ox₂ oxidation reactions, CVs for the same Au₃₈ solution at various scan rates between 100 and 1000 mV/s were recorded, Figure 3.5 (A), where the two oxidation (Ox1 and Ox2) waves in a potential window between -0.28 and 0.72 V vs. SCE, were covered. The anodic and cathodic peak currents were identical for the first two oxidation reactions.

![Cyclic voltammograms](image)

**Figure 3.5** Cyclic voltammograms of 0.1 mM Au₃₈(SC₂H₄Ph)₂₄ in 1:1 acetonitrile:benzene mixture containing 0.1 M TBAP, with the scan rate varying from (a) 50, (b) 100, (c) 200, (d) 500, and (e) 1000 mVs⁻¹.

In the cathodic scan, electrons were injected consecutively into the two degenerated LUMOs revealing the Red₁ and Red₂ waves, Figure 3.3. Similar electrochemical evaluation was performed for Red1 and Red2 reactions as above in the potential range of -0.28 to -1.22 V vs. SCE (Figure 3.6).
Figure 3.6 Cyclic voltammograms of 0.1 mM Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ in acetonitrile: benzene 1:1 mixture containing 0.1 M TBAP, scan rates varies from (a) 50, (b) 100, (c) 200, (d) 500, and (e) 1000 mVs$^{-1}$. Red$_1$ is quasi-reversible (becomes reversible at higher scan rates), which agrees with the results obtained by scanning electrochemical microscopy (SECM)\textsuperscript{8}, where a EC mechanism for Red1 with a chemical reaction (desorption of Au-thiol motifs) rate constant for the homogeneous step of 8 s$^{-1}$. In reference to Red$_2$, the ligand removal reaction following the electrochemical reduction\textsuperscript{13} is faster, and the reduction wave is irreversible at all scan rates probed. The HOMO-LUMO gap\textsuperscript{29} was determined to be 0.952 eV. This was calculated from the potential difference between the first oxidation and first reduction waves (E$^\circ_{\text{Ox1}}$ - E$^\circ_{\text{Red1}}$ = 1.158 eV) with an associated charge correction\textsuperscript{4} (Ox$_1$ and Ox$_2$ potential differences, ca. 0.206 eV). This value is close to that determined from the optical HOMO-LUMO gap (0.9 eV) following the method reported previously (see Figure 3.1).\textsuperscript{9} Figure 3.1 displays the HOMO-1 – LUMO, HOMO-2 – LUMO, and HOMO-2 – LUMO+1 transitions as well, which correlate well to those from theoretical calculations.\textsuperscript{30}
3.3.2 ECL in annihilation route

Figure 3.3 also illustrates the recorded ECL intensity versus the applied potential (ECL-voltage curve) for the same 0.1 mM Au$_{38}$ cluster electrolyte solution utilized during the potential scanning between -1.22 and 1.13 V vs. SCE. While the Au$_{38}$ has several accessible redox species with energies that in principle could react to produce ECL, no measureable ECL intensity was detected at varying potentials in this range. This is most likely due to the short lifetime and instability of all charged Au$_{38}$ species, electrogenerated during the timescale of this electrochemical scan. Consequently, it is natural to use a coreactant system that can produce strong electrogenerated oxidizing or reducing radicals that are formed at the potentials near to those of the electrogenerated Au$_{38}$ species permitting ET reactions and promoting ECL enhancement. Tri-$n$-propylamine (TPrA)$_{26, 31-32}$ and benzoyl peroxide (BPO)$_{27}$ were selected as coreactant candidates giving the well known oxidizing and reducing powers of their electrogenerated radical intermediates (vide supra).

3.3.3 ECL of the Au$_{38}$ in the presence of TPrA

Figure 3.7 displays ECL-voltage curve of the above 0.1 mM Au38 in 1:1 acetonitrile: benzene electrolyte solution with 6.3 mM TPrA at a scan rate of 100 mVs$^{-1}$. The ECL onset was at 0.810 V vs. SCE, at which the Au38 was already oxidized to Au$_{38}^{2+}$ ($E^o = 0.598$ V vs. SCE). At this potential, TPrA began to undergo an oxidation reaction (eq. 4.1) producing TPrA radical cation (TPrA$^+$), which then rapidly deprotonated to form TPrA radical (TPrA$^\cdot$) (eq. 4.2). The high reducing TPrA$^\cdot$, with a reduction power of -1.7 eV as determined by Lai and Bard,$^{26}$ injected an electron to the Au$_{38}^{2+}$ LUMO orbital (shown in the blue inset of Figure 3.7), producing the excited state, Au$_{38}^{+\ast}$ (eq. 3.3), that emitted light upon relaxing to the ground state (eq. 4.4). The ECL mechanism is very similar to that in the Ru(bpy)$_3^{2+}$/TPrA coreactant system.$^{34}$ Furthermore, ECL in the range of 0.900 and 1.200 V under the brown current segment in Figure 3.7 is attributed to Au$_{38}^{3+\ast}$/ Au$_{38}^{2+\ast}$ (most probably to Au$_{38}^{3+\ast}$, due to the
indistinguishable two-electron reaction), eqs. 3.5-8. The ECL intensity evolution and devolution followed those of TPrA•, as illustrated by the color-coded current segments in Figure 3.7.

Figure 3.7 ECL-voltage curve of the 0.1 mM Au₃₈ nanocluster in 1:1 acetonitrile: benzene mixture containing 0.1 M TBAP in the presence of 6.3 mM tri-n-propyl amine (TPrA). The insets show schematic electronic reaction diagrams of Au₃₈²⁺ and TPrA• (blue) as well as Au₃₈⁴⁺ and TPrA• (brown) to generate excited species Au₃₈⁺* and Au₃₈³⁺*, respectively.

\[
\begin{align*}
T \text{Pr} A & \rightarrow T \text{Pr} A^{\cdot*} + e^- \quad (3.1) \\
T \text{Pr} A^{\cdot*} & \rightarrow T \text{Pr} A^{\cdot} + H^+ \quad (3.2) \\
Au_{38}^{2+} + T \text{Pr} A^{\cdot} & \rightarrow Au_{38}^{\cdot*} + Pr_2 N^+ = CHCH_2CH_3 \quad (3.3) \\
Au_{38}^{\cdot*} & \rightarrow Au_{38}^{\cdot} + h\nu \quad (3.4) \\
Au_{38}^{3+} + T \text{Pr} A^{\cdot} & \rightarrow Au_{38}^{\cdot*} + Pr_2 N^+ = CHCH_2CH_3 \quad (3.5) \\
Au_{38}^{\cdot*} & \rightarrow Au_{38}^{\cdot} + h\nu \quad (3.6) \\
Au_{38}^{4+} + T \text{Pr} A^{\cdot} & \rightarrow Au_{38}^{\cdot*} + Pr_2 N^+ = CHCH_2CH_3 \quad (3.7) \\
Au_{38}^{\cdot*} & \rightarrow Au_{38}^{\cdot} + h\nu \quad (3.8)
\end{align*}
\]
The accumulated ECL spectrum (total ECL emission measured during the course of the potential scanning) revealed a very similar peak wavelength (930 nm, 1.33 eV) as that of the PL spectrum of a 0.05 mM Au_{38} clusters measured at room temperature (Figure 3.8). This apparent peak wavelength and its shape (vide infra) are due to the temperature-induced line broadening as described by Liljeroth, Quinn and co-workers.\textsuperscript{35} They elegantly showed that further luminescence peaks can be resolved at very low temperatures, with a peak at 0.98 eV related to HOMO-LUMO transition, that is hidden by other peaks at 1.15, 1.26 and 1.46 eV related to transitions from larger energy gaps. The ECL emission observed here might have a similar shape and transmissions to those of the PL process but are masked by the broadening at room temperature, while the 17 nm red shift is likely due to the self-absorption, as observed in other ECL systems.\textsuperscript{20}

Figure 3.8 (A) Accumulated ECL spectrum of the 0.1 mM Au_{38} nanocluster electrolyte solution with 6.3 mM TPrA and (B) photoluminescence spectrum of a 0.05 mM Au38 in 1:1 acetonitrile: benzene electrolyte solution. The excitation wavelength for PL was at 532 nm. Both spectra were acquired at room temperature (295 K) using an Andor BR-DD CCD camera cooled at -65 °C and attached to an Acton spectrograph.
To gain further information on the ECL mechanisms of the Au\textsubscript{38} in the presence of TPrA, we employed our newly developed spooling ECL spectroscopy that allowed us to track the ECL spectra and intensity as a function of the applied potential (i.e. time) while scanning. Figure 3.9 presents the spooling ECL spectra of the Au\textsubscript{38} with 6.3 mM TPrA, in the same potential window as the ECL-voltage curve in Figure 2 (-0.51 to 1.3 V vs. SCE). The insets demonstrate the evolution of the ECL on the anodic scan till 1.196 V (left) and the devolution for the further scanning to 1.300 V and then the return scan (right).

![Spooling ECL spectra](image)

**Figure 3.9** Spooling ECL spectra of 0.1 mM Au\textsubscript{38} nanoclusters in 1:1 acetonitrile: benzene mixture containing 0.1 M TBAP in the presence of 6.3 mM TPrA at a scan rate of 100 mV/s. The potential window was between -0.51 and 1.3 V vs. SCE and each spectrum was recorded in 1 s time interval or 100 mV potential interval. The insets show stacked spectra demonstrating the ECL evolution and devolution in course of the cyclic potential scanning.
The onset ECL spectrum with a peak wavelength of 930 nm was recorded at 0.896 V, at which potential \( \text{Au}_{38}^{3+*} \) was produced through the reaction illustrated in eq. 3.3. As the applied potential was extended to more positive potentials (e.g. 0.996 V), a resulting higher concentration of TPrA’ in the vicinity of the working electrode reacted with electrogenerated \( \text{Au}_{38}^{2+} \), leading to an enhanced ECL intensity. It is interesting to note that at higher potentials \((E > 0.994 \text{ V vs. SCE})\) at which \( \text{Au}_{38}^{2+} \) was further oxidized to \( \text{Au}_{38}^{3+} \) or \( \text{Au}_{38}^{4+} \), the ECL intensity increased 5 fold, likely due to the additional involvement of the processes outlined in eqs. 3.5-8. At 1.196 V, the ECL peak intensity reached its maximum (10 times larger than that at 0.896V), importantly at the same peak wavelength. In the reverse scan the ECL intensity decreases due to the reverse reactions as well as the resulting depletion of TPrA’ and charged \( \text{Au}_{38} \) species. The trend of ECL evolution and devolution follows that of the ECL-voltage curve in Figure 3.7. Importantly the data suggest that \( \text{Au}_{38}^{3+*} \), \( \text{Au}_{38}^{2+*} \), and \( \text{Au}_{38}^{3+*} \) likely have the same emission peak wavelength, providing additional insights into the electronic structure of \( \text{Au}_{38} \).

To examine the effect of the relative oxidation states of the \( \text{Au}_{38} \) on the luminescence intensity and wavelength, we performed an in-situ spectrophotooelectrochemical study of the 0.1 mM \( \text{Au}_{38}^0 \) solution. In this experiment, the applied potential was held at different values corresponding to the various redox states of \( \text{Au}_{38} \), illustrated in Figure 3.3. A 0.1 mM \( \text{Au}_{38} \) electrolyte solution freshly prepared under Ar atmosphere in a 1 mm thin-layer electrochemical cell. The electrolysis was performed using a Pt mesh as the working electrode, a nonaqueous reference electrode (Ag wire immersed in 0.01 M Ag\(^+\) / 0.1 M TBAP in acetonitrile), and a Pt wire as the counter electrode.\(^{12}\) The mesh electrode area was excited using a 532 nm laser, and single or spooling photoluminescence spectra were acquired from the narrow side of the thin-layer solution by means of the same CCD camera and spectrograph set. This led to the in-situ formation of the desired charge species \( \text{Au}_{38}^{3+/4+} \), \( \text{Au}_{38}^{2+} \), \( \text{Au}_{38}^{+} \), \( \text{Au}_{38}^{-} \), and \( \text{Au}_{38}^{2-} \) at 1.0 V, 0.65 V, 0.45 V, -0.85 and -1.1 V vs. SCE, respectively (Figure 3.10B-F). At the same time, spooling PL spectra of the solution were recorded during the electrolysis to help track possible changes in the PL emission wavelength and intensity. Figure 3.10
shows the PL spectra of the different charge species Au$_{38}^{z}$ ($z= 0$ (A), 1+ (B), 2+ (C), 3+/4+ (D), 1- (E), and 2- (F),) and the insets illustrate the typical spooling PL spectra accumulated during the electrolysis. It is evident that there is no significant peak wavelength change as we progress from one charge state to the next, except that of the Au$_{38}^{-}$ blue-shifted, while the intensity of the PL emission does vary with the charge. Importantly, from Au$_{38}^{0}$ to Au$_{38}^{2+}$ and Au$_{38}^{2+}$ there is no notable change in the recorded PL intensity (PLint. $\sim$ 12 Kcps), while Au$_{38}^{3+}$/Au$_{38}^{4+}$ shows a decrease to $\sim$ 9 Kcps. The Au$_{38}^{-}$ revealed the highest intensity up to 26 Kcps at the end. This could be due to its electronic configuration with one electron in each LUMO, which leads higher probability of transition back to the only HOMO having a vacancy of one electron. Finally, the Au$_{38}^{2-}$ showed basically no change in the course of its formation.
Figure 3.10 PL spectra of the $\text{Au}^{z-}_{38}$ ($z=\text{-2, -1, 0, 1, 2, 3/4+}$) in 1:1 acetonitrile:benzene mixture containing 0.1 M TBAP using a 1 mm thin layer spectroelectrochemical cell (see experimental). The applied potential was scanned in a range as indicated in each panel, corresponding to (A) $\text{Au}^{0}_{38}$, (B) $\text{Au}^{+}_{38}$, (C) $\text{Au}^{2+}_{38}$, (D) $\text{Au}^{3+/4+}_{38}$, (E) $\text{Au}^{-}_{38}$, and (F) $\text{Au}^{2-}_{38}$. The insets demonstrate the typical spooling PL spectra in course of the corresponding electrolysis processes in a time interval of 50 s for approximate 13 min. The arrows indicate the electrolysis time and spooling direction. All samples were excited with a 532 nm laser source.
The Au$_{38}$/TPrA coreactant system was further studied by varying the concentration of TPrA ([TPrA]) from 12.5, to 25, 50, 100 and 200 mM. With the increased [TPrA], the amount of TPrA$^\cdot$ was augmented in the vicinity of the electrode at the same potential, thus an increase in ECL intensity was expected. The highest ECL intensity was observed in the presence of 50 mM TPrA, Figure 3.11. The onset ECL-voltage curve was at 0.850 (Figure 3.12) while that in the spooling ECL spectra (Figure 3.11) was discovered at 0.900 V vs. SCE.

![ECL-Voltage curve](image)

**Figure 3.11** ECL-Voltage curve of the 0.1 mM Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ in 1:1 acetonitrile:benzene mixture containing 0.1 M TBAP in the presence of 50 mM tri-$n$-propylamine.

The ECL spectra acquired over the potential scanning remained a constant peak wavelength at 930 nm, indication of similar ECL mechanisms as in the case of Figure 3.8. The [TPrA] has no appreciable effect on the ECL generation pattern of the coreactant system. Importantly, the ECL peak height with 50 mM TPrA at 1.200 V vs. SCE is four times higher than that with 6.3 mM TPrA, expected for the generation of a higher concentration of the TPrA radical with increased [TPrA].
Figure 3.12 Spooling ECL spectra of the 0.1 mM Au38 in 1:1 acetonitrile:benzene mixture containing 0.1 M TBAP with 50 mM TPrA at a scan rate of 100 mV/s. The potential window was between -0.51 and 1.3 V vs. SCE and each spectrum was recorded in 1 s time interval. The insets show stacked spectra illustrating ECL evolution and devolution during the potential scanning.

The ECL-voltage curves along with corresponding spooling ECL spectra of the Au38 solution in the presence of 12.5, 25, 100 and 200 mM TPrA are shown in the SI (Figures S 3.1-4). No appreciable peak wavelength change was observed. In the TPrA concentration range between 6.5 mM and 50 mM, the higher the TPrA′, the faster the reaction rate of the electrogenerated Au38 charged species with TPrA′ at the same potentials, thus the higher concentration of the excited states and the brighter the ECL intensity. The ECL intensity drops if the TPrA concentration is higher than 50 mM, indicating possible quenching of ECL by the TPrA coreactant at very high concentrations; an effect observed in other ECL systems using this coreactant.26
Figure 3.13 Accumulated ECL spectra for various [TPrA] from 6.3 (A) to 12.5 (B), 25 (C), 50 (D), 100 (E) and 200 (F) mM.

The accumulated ECL spectra (A-F) in the presence of TPrA concentrations of 6.2 to 200 mM are shown in Figure 3.13, which were obtained for two successive cycles of potential scanning between -0.51 to 1.3 V vs. SCE. It can be noticed that the ECL emissions have the same peak wavelength (930 nm), as confirmed by the spooling experiments. These results are in good agreement with the observed spooling PL spectra obtained through in-situ electrolysis.

Figure 3.14 illustrates a good correspondence between the integrals of ECL-voltage curves (black, Figures 3.7 and S 3.1-4) vs. time and of the accumulated ECL spectra (red, Figures 3.8, 3.11, S 3.1-4) vs. wavelength in the presence of various [TPrA]. It is worth noting that the highest ECL emission was reached in the presence of 50 mM TPrA, while further increased [TPrA] to 100 and 200 mM decreased ECL intensity, mainly due to the quenching effect caused by the high concentration of the coreactant. The ECL efficiency of the Au_{38}/TPrA system was calculated versus Ru(bpy)_{3}^{2+}/TPrA system and shown in Table 3.1 (see the experimental for the methodology). It is exciting...
to note that a high relative ECL efficiency of > 350% was obtained with 50 mM TPrA, disregarding higher values with 100 and 200 mM TPrA. Since the Andor iDUS BR-DD CCD camera has a very similar response sensitivity for both the Ru(bpy)$_3^{2+}$ (emission at 650 nm) and Au$_{38}$ (emission at 930 nm), our ECL efficiency measurements should be very reliable. In contrast, our conventional ECL efficiency determination using a PMT underestimated the values, due to the dramatic depleted PMT sensitivity in the NIR region (see Appendices for details) with wavelength longer than 830 nm.

Table 3-1 Calculated ECL efficiency for the Au$_{38}$/TPrA system with various [TPrA] in reference to that of Ru(bpy)$_3^{2+}$/TPrA in 1:1 acetonitrile: benzene electrolyte solution (absolute quantum ECL efficiency of Ru(bpy)$_3^{2+}$ is 0.05).

<table>
<thead>
<tr>
<th>[TPrA]/ mM</th>
<th>ECL eff. %</th>
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<tr>
<td>6.3</td>
<td>13</td>
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<td>12.5</td>
<td>24</td>
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<td>25</td>
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<td>50</td>
<td>354</td>
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<tr>
<td>100</td>
<td>591</td>
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<tr>
<td>200</td>
<td>836</td>
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</tbody>
</table>
Figure 3.14 Integrals of ECL-voltage curves (acquired using the PMT) vs. time (black) and ECL intensity (measured by the CCD camera and spectrograph set) vs. wavelength (red) in the presence of various [TPrA]. These integrated values are equivalent to the numbers of photons emitted.

3.3.4 ECL of the Au$_{38}$/BPO coreactant system

Based on the two consecutive electrochemical reduction reactions of the Au$_{38}$ in the cathodic region, it is also of interest to investigate ECL emission in the presence of BPO, from which a strong oxidizing intermediate, benzoate radical ($C_6H_5CO_2^\cdot$) with a reduction potential of 1.5 V (eq. 3.9), can be produced. In addition, we have recently reported the ECL of the Au$_{25}$(SR)$_{18}$ cluster/BPO system. Among various organic soluble coreactant in ECL studies, BPO have been used extensively mainly due to its solubility in majority of organic solvents.

$$BPO + e \rightarrow C_6H_5CO_2^\cdot + C_6H_5CO_2^- \quad (3.9)$$
Figure 3.15A illustrates cyclic voltammogram and ECL-voltage curve of 0.1 mM Au$_{38}$ clusters in the presence of 5 mM BPO in 1:1 acetonitrile: benzene mixture. The CV shows a reduction peak at ~ -1.5 V vs. SCE, at which C$_6$H$_5$CO$_2$\(^{\cdot}\) was generated in the vicinity of the working electrode (eq. 3.9). The ECL onset was at -1.0 V vs. SCE, indicating electronic interaction between negatively charged species of the Au$_{38}$, and C$_6$H$_5$CO$_2$\(^{\cdot}\). By comparing the reduction potentials of Au$_{38}^{0/\cdot}$ (eq. 3.10) and Au$_{38}^{\cdot/2\cdot}$ (eq. 3.11) with the onset potential value, it can be noticed that at -1.0 V, the C$_6$H$_5$CO$_2$\(^{\cdot}\) reacted with Au$_{38}^{2\cdot}$ (eq. 3.12). In fact, the C$_6$H$_5$CO$_2$\(^{\cdot}\) accepts an electron from one of the two Au$_{38}^{2\cdot}$ HOMO orbital (the inset in Figure 3.3), producing the Au$_{38}^{\cdot\cdot}$ excited state. The Au$_{38}^{\cdot\cdot}$ then relaxed to the ground state, emitting light (eq. 3.13). The acquired ECL spectrum displayed a peak wavelength of 930 nm (Figure 9B), very close to what we observed for the Au$_{38}$/TPrA system. The ECL peak maximum in the ECL-voltage curve was found to be at -1.345 V vs. SCE, at which the Au$_{38}$ cluster was reduced all the way to Au$_{38}^{2\cdot}$ and the C$_6$H$_5$CO$_2$\(^{\cdot}\) reached its maximum concentration in the vicinity of the working electrode. Thus, electron removal from Au$_{38}^{2\cdot}$ HOMO orbitals formed Au$_{38}^{\cdot\cdot}$ (eq. 3.12). The ECL enhancement is related to the high concentrations of both electrogenerated C$_6$H$_5$CO$_2$\(^{\cdot}\) and Au$_{38}^{2\cdot}$. 
Figure 3.15 (A) Cyclic voltammogram (red) and ECL-voltage curve (teal) of the 0.1 mM Au$_{38}^+$ electrolyte solution in the presence of 5 mM benzoyl peroxide (BPO). (B) The accumulated ECL spectrum of the same solution recorded on an Andor BR-DD CCD camera cooled at -65°C and attached to an Acton spectrograph.

\[ \text{Au}_{38}^0 + e \rightarrow \text{Au}_{38}^- \]  \hspace{1cm} (3.10)

\[ \text{Au}_{38}^- + e \rightarrow \text{Au}_{38}^{2-} \]  \hspace{1cm} (3.11)

\[ \text{Au}_{38}^{2-} + C_6H_5CO_2^- \rightarrow \text{Au}_{38}^{*} + C_6H_5CO_2^- \]  \hspace{1cm} (3.12)

\[ \text{Au}_{38}^{*} \rightarrow \text{Au}_{38}^- + h\nu \]  \hspace{1cm} (3.13)

The ECL peak wavelength is again in good agreement with that of PL spectrum shown in Figure 3.16.
This similarity in the peak wavelength suggests that the related ECL and PL relaxation processes and emission through HOMO-LUMO orbitals. The formed $\text{Au}_{38}^{-}$ might participate in a catalytic reaction and get reduced again on the electrode surface. The reduction waves of $\text{Au}_{38}^{-}$ to $\text{Au}_{38}^{2-}$ are less negative than that for $\text{C}_6\text{H}_5\text{CO}_2\cdot^\text{radical}$ formation. One can argue that this is the main reason for the lower ECL light emission intensity of the $\text{Au}_{38}/\text{BPO}$ system, while close potentials for the formation of TPrA radical and $\text{Au}_{38}^{2+}$ and $\text{Au}_{38}^{3+/4+}$, result in higher ECL intensity. The ECL efficiency relative to the $\text{Ru(bpy)}_3^{2+/3+/4+}$/BPO system was determined to be 7.2 %, which was much lower than that of the $\text{Ru(bpy)}_3^{2+/3+/4+}$/TPrA system. Higher concentrations of BPO were also

Figure 3.16 (A) Accumulated ECL spectrum of 0.1 mM $\text{Au}_{38}$ with 5 mM BPO and (B) photoluminescence spectrum of 0.05 mM $\text{Au}_{38}$ in 1:1 acetonitrile: benzene mixture.
tested. No ECL emission was observed, due to the quenching of ECL by high BPO concentration.\textsuperscript{37}

3.4 Conclusions

For the first time the ECL of the Au\textsubscript{38} cluster is reported, displaying a unique peak wavelength at 930 nm in the NIR region. The results suggest all accessible excited states of Au\textsubscript{38} cluster emit at the same wavelength, which was unambiguously corroborated from the \textit{in-situ} spectrophotoelectrochemistry. It was also revealed that among the charged Au\textsubscript{38} species, the Au\textsubscript{38}\textsuperscript{-} generates the highest PL intensity. The short lifetime of both the electrogenerated Au\textsubscript{38}\textsuperscript{2-} and Au\textsubscript{38}\textsuperscript{3+/4+} species or their reactivity limited ECL emission in the annihilation route. Coreactants such as TPrA and BPO greatly enhanced the ECL emissions. Spooling ECL spectroscopy confirmed that Au\textsubscript{38}\textsuperscript{+*} (and Au\textsubscript{38}\textsuperscript{3+*}) and Au\textsubscript{38}\textsuperscript{-*}, were involved in the ECL emission processes in the presence of TPrA and BPO, respectively. Also, the accumulated ECL spectra showed that ECL emission peak wavelengths, at \textasciitilde930 nm in NIR region, does not change by altering the TPrA concentration or the applied potential. Interestingly, the ECL intensity can be tuned by changing the coreactant concentration or working electrode potential. ECL efficiency was determined to be 3.5 time higher than that of the Ru(bpy)\textsubscript{3}\textsuperscript{2+/TPrA} system. It is anticipated that the NIR-ECL of the Au\textsubscript{38} clusters will find electroanalytical applications in imaging of live cells.

3.5 References


Chapter 4

4 Near-infrared electrochemiluminescence from \( \text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}^+ \) clusters co-reacted with tri-\( n \)-propylamine

- This Chapter published as a communication. The corresponding reference is: Mahdi Hesari, Mark S. Workentin, and Zhifeng Ding, *RSC Advances*, **2014**, 4, 29559-29562.

- All of the schemes, figures, and text in Chapter 4 reprinted with permission from *RSC Advances*. **2014**, 4, 29559-29562, Copyright 2014 Royal Society of Chemistry.
4.1 Introduction

The Au$_{25}$(SR)$_{18}^z$ cluster family (Au$_{25}^z$, $z$ =1−, 0 and 1+) has been shown to possess a number of interesting optical and electrochemical properties that are dependent on the charge states. This should be very interesting and useful in electrochemiluminescence (ECL). Near-infrared (NIR) ECL of Au$_{25}$ clusters can be observed from electron transfer (ET) between electrogenerated radicals, which might find great applications in desired in vivo bio-imaging. Recently, we examined the ECL of the Au$_{25}^+$ through annihilation of electrogenerated Au$_{25}^{2+}$ and Au$_{25}^{2-}$ species. The result showed very weak ECL similar to that of visible ECL of Au$_{25}^-$ clusters in aqueous solution, most likely due to their short lifetime within the experiment time scale. Furthermore, enhanced ECL originated from Au$_{25}^{-*}$ upon relaxation to its ground state was observed in the benzoyl peroxide (BPO) co-reactant system, where Au$_{25}^{2-}$ reacted with the benzoate radical (a strong oxidizing agent with $E^\circ > +1.5$ V vs. SCE) generated via the reduction of both Au$_{25}^{2+}$ and BPO. To further explore and elucidate possible ECL emissive states and mechanisms, the system of Au$_{25}^+$ clusters in the presence of tri-$n$-propyamine (TPrA) should be very interesting. A number of Au$_{25}$ oxidation states including Au$_{25}^{2+}$, Au$_{25}^+$, Au$_{25}^0$, Au$_{25}^-$ and Au$_{25}^{2-}$ can be easily accessed and a highly reducing TPrA radical (TPrA$^*$, $E^\circ = -1.7$ V vs. SCE) can be generated by quickly deprotonating the intermediate, TPrA$^{+*}$ after the oxidation of TPrA. Multiple excited states such as Au$_{25}^{++*}$, Au$_{25}^{0*}$ and Au$_{25}^{-*}$ are anticipated to be produced by interactions of Au$_{25}^{2+}$, Au$_{25}^+$ and Au$_{25}^0$ with TPrA$^*$, respectively. Unlike BPO, TPrA is more compatible with both aqueous and organic solvents, a desirable feature for many applications.

In this chapter, I will discuss the ECL of the Au$_{25}^+$ and TPrA co-reactant system, where ECL was interrogated by changing the TPrA concentration, [TPrA], and applied potential at the working electrode. We employed our newly developed spooling ECL spectroscopy to correlate the ECL spectra with the applied potential. As a result, we were able to elucidate ECL mechanisms and assign the excited states of the Au$_{25}$ responsible for the observed ECL, namely Au$_{25}^{+*}$, Au$_{25}^{0*}$ and
Importantly, the ECL intensity in the TPrA co-reactant system was 14 times higher than observed that with BPO, due in part to the reduction power TPrA$^+$.\(^{15}\)

### 4.2 Experimental

#### 4.2.1 Chemicals

Hydrogen tetrachloroaurate trihydrate (Aldrich, 99.9%), phenylethanethiol (Aldrich, 98%), tetraoctylammonium bromide (Aldrich, 98%), sodium borohydride (Aldrich, 99%), hydrogen peroxide (Caledon, 30%), sodium hydroxide (Caledon, 99%), tetrahydrofuran (Caledon, 99.9%), pentafluorobenzoyl chloride (Alfa Aesar, 99%), methanol (Caledon, 99.8%), dichloromethane (Caledon), chloroform (Caledon, 99.8%), ethanol (Caledon, 99.8%), and acetonitrile (Caledon) were used as received. Deuterated chloroform and dichloromethane was furnished by Cambridge Isotope Laboratories. For the electrochemical experiments benzene (tore seal), acetonitrile (tore seal) and terabutylammonium bromide (99%) were purchased from Aldrich.

#### 4.2.2 Synthesis of \(\text{Au}_{25}(\text{S(CH}_2\text{)}_2\text{Ph})_{18}^-\cdot\text{TOA}^+\) and \(\text{Au}_{25}(\text{S(CH}_2\text{)}_2\text{Ph})_{18}^+\cdot\text{C}_6\text{F}_5\text{CO}_2^-\) (\(\text{Au}_{25}^+\))

TOA$\cdot$Au$_{25}$(SC$_2$H$_4$Ph)$_{18}$ has been synthesized following published procedures.\(^8\) Briefly, 2.54 mmol HAuCl$_4$$\cdot$3H$_2$O and 3.04 mmol tetra-$n$-octylammonium bromide (TOABr) were co-dissolved in 100 mL THF. The dark red solution was put in the ice-bath for 30 min and then 15.67 mmol of phenylethane thiol was added one drop at a time over 10 minutes. Meanwhile, the color of mixture turned yellowish while the ice bath was kept for 2 hours. The solution was heated up to room temperature and led to a colorless solution after 3 hours. At this point, the ice bath was put back and 26.69 mmol NaBH$_4$, dissolved in 20 mL of ice-cold distilled water was added to the mixture quickly under vigorous stirring. A dark solution formed with the addition of the reducing agent. The solution was gravity filtered and the solvent volume was vacuum evaporated. The
residual was settled down overnight. The excess of NaBH₄ and phenylethane thiol was removed by washing the crude sample with water/ethanol mixture. The final product was extracted from -(Au-S-Au-S)-oligomer using acetonitrile to get an oily product, which then recrystallized to obtained a dark-brown needle crystals.

To convert the Au₂₅⁻ to the Au₂₅⁺, bis(pentafluorobenzoyl) peroxide was used as oxidizing agent. Synthesis of bis(pentafluorobenzoyl) peroxide⁸ was performed by following Barson’s procedure with some modification¹⁶. Then, the purity of the sample was checked by TLC (15:1 petroleum ether/ethyl acetate) and ¹⁹FNMR (-133.74, -143.30, -158.15 ppm in CDCl₃).

Upon addition of the peroxide to the Au₂₅(SC₂H₄Ph)₁₈⁻ an oxidation reaction can happen via electron transfer between the clusters and the peroxide, which leads to formation Au₂₅(SC₂H₄Ph)₁₈⁺C₆F₅CO₂⁻ cluster. In our work, the same methodology has been applied to get “1+” monodispersed cluster. Briefly, 1 mmol of crystallized Au₂₅⁻ was prepared in d₂-dichloromethane in an NMR tube and ¹HNMR spectrum was recorded. Then 2 mmol of the peroxide in CD₂Cl₂ was added to the above solution.

4.2.3 Characterizations of Au₂₅(S(CH₂)₂Ph)₁₈⁺C₆F₅CO₂⁻ (Au₂₅⁺)

The UV-Vis-NIR (Figure 4.1) spectrum of Au₂₅(S(CH₂)₂Ph)₁₈⁺C₆F₅CO₂⁻ was taken to monitor the reaction completion and purity of the final product. The three peaks at 387, 467, 656 nm are distinct UV-Vis-NIR features of Au₂₅(S(CH₂)₂Ph)₁₈⁺C₆F₅CO₂⁻. The intensity and peak positions of this Au₂₅ charge state can be used to differentiate with other charged Au₂₅ clusters.
Figure 4.1 UV-Vis-NIR absorption spectrum of synthesized $\text{Au}_{25}^+$ in dichloromethane.

Also, $^{1}H$ NMR spectrum of the $\text{Au}_{25}(\text{S(CH}_2\text{)}_2\text{Ph})_{18}^{+}.\text{C}_6\text{F}_5\text{CO}_2^-$ is shown in Figure 4.2. It can be noticed that the peaks corresponding to the presence of tetra-$n$-octylammonium are present in the solution due to that fact that $\text{Au}_{25}(\text{S(CH}_2\text{)}_2\text{Ph})_{18}^-$.TOA$^+$ was used as the starting material. The obtained spectrum indicates the complete conversion of $\text{Au}_{25}(\text{S(CH}_2\text{)}_2\text{Ph})_{18}^-$.TOA$^+$ to $\text{Au}_{25}(\text{S(CH}_2\text{)}_2\text{Ph})_{18}^+.\text{C}_6\text{F}_5\text{CO}_2^-$, while there is no trace of the starting material or half-oxidation of the nanocluster to $\text{Au}_{25}(\text{S(CH}_2\text{)}_2\text{Ph})_{18}^0$. It worth noting that proton NMR spectrum of $\text{Au}_{25}(\text{S(CH}_2\text{)}_2\text{Ph})_{18}^0$ shows an identical peak at 5.15 nm (Please see Figure 5.1)
Figure 4.2 $^1$H NMR spectrum of synthesized Au$_{25}^+$ in $d_2$-dichloromethane. Residual solvent peak at 5.32 ppm.

MALDI-TOF mass spectrum also proved that the original cluster exist over the course of reaction. To run the MALDI experiment, the sample was mixed with trans-2-[3-(4-tert-butylyphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB), applying 1000/0.2 ratio of matrix/analyte and 7 mL of the prepared sample was placed on the target plate, dried at room temperature. The laser intensity was kept as low as possible to have a good signal to noise ratio, although some fragmentation observed among the sample analysis. (Figure 4.3)
Figure 4.3 MALDI-TOF mass spectrum of Au$_{25}$(SC$_2$H$_4$Ph)$_{18}^+$. The low intensity peak are corresponding to the fragments.

4.2.4 Spectroelectrochemistry of Au$_{25}$(SC$_2$H$_4$Ph)$_{18}^+$

The photoluminescence spectra of different Au$_{25}$ charge states were obtained in the course of spectroelectrochemistry while a 1 mM Au$_{25}^-$ solution containing 0.1 M TBAP in 1:1 acetonitrile: benzene solution was excited using 532 nm laser, and spectra were recorded with an Andor BR-DD CCD camera (cooled at -65°C) attached to an Acton spectrograph. A long-pass edge filter was placed between the sample and the detector to cut the excitation peak in the PL spectrum. In situ spectroelectrochemical measurements were conducted with a commercially available thin layer quartz cell from BASi connected to a CHI610 potentiostat with a three-electrode configuration. The electrolysis was performed using a nonaqueous reference electrode (Ag/Ag$^+$ reference electrode (0.01 M AgNO$_3$ and 0.1 M TBAP in acetonitrile), a Pt mesh and Pt wire as the working and counter electrodes.17-18
ECL efficiency values were obtained by comparing the integrated ECL intensities (equivalent to the number photons) and the current values (charges) of the Au\(_{25}^{+/+}\)/TPrA samples with those of the Ru(bpy)\(_3^{2+/+}\)/TPrA system. The quantum yield was calculated using the below equation:

\[
\phi_X = 100 \times \left( \frac{\int_a^b ECL \, dt}{\int_a^b \text{Current} \, dt} \right) / \left( \frac{\int_a^b ECL \, dt}{\int_a^b \text{Current} \, dt} \right)_S
\]

where \(\Phi\) is the quantum yield (%) relative to the Ru(bpy)\(_3^{2+/+}\)/TPrA system, ECL is the ECL intensity, current is the electrochemical current value, St is the standard (the Ru(bpy)\(_3^{2+/+}\)/TPrA) and \(x\) is the sample (the Au\(_{25}^{0/0}\)/TPrA). Table 4-1 shows calculated values for each TPrA concentration.

### 4.3 Results and Discussion

#### 4.3.1 Electrochemistry of Au\(_{25}(SC_2H_4Ph)^{+}\)C\(_6\)F\(_5\)CO\(_2^-\) clusters

The cyclic voltammogram started at open circuit potential value (0.558 V) (Figure 4.4). During the anodic scanning of the applied potential, an irreversible peak at \(E^{\circ'}(\text{Au}_{25}^{2+/+}\text{Au}_{25}^{+}) = 0.817 \, \text{V}\) vs. SCE corresponding to the electron(s) removal from the HOMO orbitals. Towards the reverse scan two quasi-reversible reduction waves are observed with \(E^{\circ'}(\text{Au}_{25}^{+}/\text{Au}_{25}^{0}) = 0.185 \, \text{V}\) and \(E^{\circ'}(\text{Au}_{25}^{0}/\text{Au}_{25}^{-}) = -0.06 \, \text{V}\) vs. SCE. These correspond to the Au\(_{25}^{+}\) clusters being reduced consecutively to Au\(_{25}^{0}\) and then Au\(_{25}^{-}\). The energy difference to convert Au\(_{25}^{+}\) to Au\(_{25}^{-}\) via the two successive electrons is 0.245 eV. At more negative potentials there is a broad irreversible reduction wave with an estimated half-wave potential of -1.437 V vs. SCE corresponding to the further reduction of Au\(_{25}^{-}\) clusters to Au\(_{25}^{2-}\). This reduction injects an electron into the LUMO making Au\(_{25}^{2-}\) less stable.
Figure 4.4 Cyclic voltammogram of 0.1 mM Au\textsubscript{25}\textsuperscript{+} in 1:1 acetonitrile: benzene mixture, containing 0.1 M TBAP as the supporting electrolyte, scan rate: 100 mV/s. The arrow shows potential scanning direction, the cross indicates initial potential.

4.3.2 Electrogenenerated chemiluminescence of Au\textsubscript{25}(SC\textsubscript{2}H\textsubscript{4}Ph)\textsuperscript{+}C\textsubscript{6}F\textsubscript{5}CO\textsubscript{2}\textsuperscript{-} clusters

It is important to keep in mind the two formal redox potentials, $E^\circ'(\text{Au}_{25}^+/\text{Au}_{25}^0) = 0.185 \text{ V}$ and $E^\circ'(\text{Au}_{25}^{2+}/\text{Au}_{25}^+) = 0.817 \text{ V vS. SCE}$ (see Figure 4.4). In a typical ECL experiment, a 0.1 mM solution of the Au\textsubscript{25}\textsuperscript{+} was prepared in 1:1 acetonitrile: benzene mixture containing 0.1 M tetra-\textit{n}-butylammonium perchlorate (TBAP) as the supporting electrolyte in a glovebox using airtight cylindrical glass cell with a flat Pyrex window at the bottom for the ECL detection. To this solution a specific concentration of TPrA was added under Ar atmosphere blanket; the [TPrA] was varied from 6.3, to 12.5, 25, 50, 100, and 200 mM in order to gain insight into mechanistic details on the excited states responsible for the ECL emissions observed upon oxidation of both TPrA and Au\textsubscript{25}\textsuperscript{+}.

Figure 4.5 shows the cyclic voltammogram (CV) and ECL-voltage curve of a 0.1 mM Au\textsubscript{25}\textsuperscript{+} electrolyte solution with 50 mM TPrA at a scan rate of 100 mVs\textsuperscript{-1}. 92
Figure 4.5 (A) Cyclic voltammogram of 0.1 mM solution of Au$_{25}^+$ in 1:1 benzene:acetonitrile mixture containing 0.1 M TBAP in the presence of 50 mM TPrA scanning between -0.482 to 1.216 V, along with (B) ECL-voltage curve recorded by the PMT at a scan rate of 100 mVs$^{-1}$. (C) ECL Integral of each spooling ECL spectrum in Fig. 1 vs. the applied potential.

The CV (black in Figure 4.5) demonstrates the dominating irreversible oxidation of TPrA to TPrA$^+$ with a peak potential of 0.880 V vs. SCE (eq. 3.1). The TPrA$^+$ intermediate deprotonates rapidly forming TPrA$^*$ (eq. 3.2). The red curve in Figure 4.5B is the corresponding ECL-voltage curve, illustrating the ECL...
intensity as a function of applied potential. The onset of ECL occurred at 0.643 V, a potential at which the electrogenerated TPrA$^*$ reacted with Au$_{25}^+$ in the bulk solution and produced ECL light from the formed Au$_{25}^0*$ excited state (eqs. 3.4).

\[
T \text{PrA} \rightarrow T \text{PrA}^{*+} + e 
\]
\[
T \text{PrA}^{*+} \rightarrow T \text{PrA}^* + H^+ 
\]
\[
\text{Au}_{25}^+ + T \text{PrA}^* \rightarrow \text{Au}_{25}^{0*} + T \text{PrA}^* 
\]
\[
\text{Au}_{25}^{0*} \rightarrow \text{Au}_{25}^0 + h\nu_1 
\]

Figure 4.6 demonstrates the spooling ECL spectra acquired at a time interval of 1 s or a potential interval of 100 mV for the above solution during a cycle of the potential scanning between -0.557 and 1.142 V at a scan rate of 100 mVs$^{-1}$.

**Figure 4.6** Spooling ECL spectra of 0.1 mM of Au$_{25}^+$ with 50 mM TPrA during the potential scanning between -0.557 and 1.142 V at a scan rate of 100 mVs$^{-1}$. Insets present stack spectra showing ECL evolution and devolution.

The onset ECL spectrum was also at 0.643 V, which is identical to that from the ECL-voltage curve in Figure 4.5B. The onset peak wavelength reads 872 nm in Figure 4.6. The measured photoluminescence (PL) spectrum of electrogenerated
shown in Figure 4.7 confirms that the PL emission at 865 nm belongs to the 
\(\text{Au}_{25}^0\) excited state.

![Photoluminescence spectra](image)

**Figure 4.7** Photoluminescence spectra of 0.1 mM \(\text{Au}_{25}^-\) (red curve), and \(\text{Au}_{25}^+\) (brown curve), \(\text{Au}_{25}^0\) (green curve) electrogenerated in the 1:1 acetonitrile: benzene electrolyte solution. The thin layer of the spectroelectrochemical cell was excited using 532 nm laser, and the spectra were recorded with an Andor BR-DD CCD camera (cooled at \(-65^\circ\text{C}\)) attached to an Acton spectrograph.

The slight difference between the ECL and PL wavelengths is due to the self-absorption (inner-filter effect).\(^{20}\) The ECL peak wavelength remained the same when the potential was scanned towards more positive potentials. At 0.743 V, for instance, the intensity is augmented due to the increasing [TPrA\(^-\)]. This is an indication of the same excited state generated via electron transfer from TPrA\(^-\) (\(E^o = -1.7\ \text{eV}\))\(^{15}\) to the LUMO of \(\text{Au}_{25}^+\) (eqs. 4.3-4). Possible electron transfer to the \(\text{Au}_{25}^+\) HOMO would not lead to any excited state. Also, at these potentials the \(\text{Au}_{25}^0\) formed would be re-oxidized to \(\text{Au}_{25}^+\) leading to the electrocatalytic process (EC\(^+\)) for ECL.\(^{21}\) At potentials more positive than 0.847 V (larger than \(E^o\) (\(\text{Au}_{25}^{2+}/\text{Au}_{25}^{+}\))
Au$_{25}^{+}$), 0.817 V), at which Au$_{25}^{2+}$ was generated in the vicinity of the working electrode. Au$_{25}^{+}$* was expected to be produced via interaction of Au$_{25}^{2+}$ with TPrA* (eqs. 4.5-6). The same peak wavelength of 872 nm was observed, Figure 4.6. In contrast, the ECL intensity was increased dramatically. These agree well with the observations from the *in-situ* PL spectroscopy of the three species generated via thin layer electrolysis in the same electrolyte solution (Figure 4.7). The PL lead to the conclusion that Au$_{25}^{0}$* and Au$_{25}^{+}$* have almost an identical emission peak wavelength (865 and 860 nm, respectively) but Au$_{25}^{+}$* has stronger emission light intensity. The above results validated our ECL reaction mechanism for the Au$_{25}^{+}$* generation and then light emission, eqs. 4.5-6. The ECL intensity at 0.847, 0.947 and 1.047 increased to 27, 34 and 36 times of that at 0.643 V. Not only was the Au$_{25}^{+}$* a stronger emitter than the Au$_{25}^{0}$* but also the oxidation of TPrA (with a peak potential of 0.880 V) was centred in this potential region, leading to a high [TPrA*]. The combination of the two factors brought an ECL enhancement. The ECL peak intensity dropped gradually upon potential scanning to a little further positive potential (1.142 V) and back to 0.541 V. The depletion of the [TPrA*] caused a decrease in [Au$_{25}^{+}$*] or a switch to Au$_{25}^{0}$*, and therefore a diminishing light emission. The ECL devolution can be clearly seen in the right inset in Figure 4.6. The spooling ECL spectra give more information than ECL-voltage curve, Figure 4.5.

\[
\begin{align*}
Au_{25}^{2+} + TPrA^* & \rightarrow Au_{25}^{+} + TPrA^* \\
Au_{25}^{+} & \rightarrow Au_{25}^{+} + hv 
\end{align*}
\] (4.5) (4.6)

Figure 4.8 shows the spooling ECL spectra of Au$_{25}^{+}$ (0.1 mM) in the presence of 100 mM TPrA in a very similar potential region.
Figure 4.8 Spooling ECL spectra of 0.1 mM of \( \text{Au}_{25}^{+} \) with 100 mM TPrA during the potential scanning between -0.554 and 1.146 V at a scan rate of 100 mVs\(^{-1}\). Insets represent stack spectra demonstrating ECL evolution and devolution.

The increased [TPrA] promoted a very high local [TPrA\(^{-}\)] in the vicinity of the working electrode biased with an anodic potential. The onset ECL with 100 mM TPrA was delayed for 100 mV relative to that with 50 mM TPrA, which might be caused by the quenching of excited state by TPrA. This is a phenomena also observed with \( \text{Ru(bpy)}_{3}^{2+} \) and other co-reactant systems.\(^{14}\) More importantly, the ECL peak wavelength showed a pronounced red shift to 945 nm, Figure 4.8, which was maintained the same in the ECL evolution and devolution as illustrated by the recorded spooling ECL spectra. Again, the PL spectrum of \( \text{Au}_{25}^{-} \) produced via electrolysis shows a peak wavelength at 945 nm with similar PL intensity to that of \( \text{Au}_{25}^{0} \), Figure 4.7. This means that \( \text{Au}_{25}^{-*} \) species can be differentiated by the longer peak wavelength from \( \text{Au}_{25}^{0*} \) and \( \text{Au}_{25}^{+*} \). Our PL results agree well with those reported by Kauffman and Jin et al. upon electrolysis of \( \text{Au}_{25}^{-} \).\(^{17-18}\) With the increased [TPrA\(^{-}\)], it is plausible that ECL in Figure 4.8 is due to the formation of \( \text{Au}_{25}^{-*} \) that emitted light upon relaxation to its ground state. The strong reducing agent, TPrA\(^{-}\) must act as an electron carrier to drive reduction reactions of \( \text{Au}_{25}^{+} \) (in the bulk at the ECL onset potential) and \( \text{Au}_{25}^{2+} \) (generated at the electrode biased with more positive potentials) to \( \text{Au}_{25}^{0} \), and all the way to \( \text{Au}_{25}^{2-} \) (eqs. 7-9).
It is worth noting that the alternative route could be the reduction of \( \text{Au}_{25}^{n} \) \((n=1^+ \text{ and } 0)\) by the TPrA radical, and eventually \( \text{Au}_{25}^{n-1} \) will form. \( \text{Au}_{25}^{-} \) was formed either via electron transfer from TPrA\(^{•} \) to the \( \text{Au}_{25}^{0} \) LUMO (eq. 10) or that from \( \text{Au}_{25}^{2^-} \) HOMO to \( \text{Au}_{25}^{0} \) HOMO (eq. 11). \( \text{Au}_{25}^{-} \) then relaxed to the ground state, emitting at the peak wavelength of 945 nm (eq. 12). It is interesting to notice that the ECL intensity measured in the unit of counts per second (cps) with 100 mM [TPrA] (Figure 4.8) were lower than those with 50 mM [TPrA] (Figure 4.8) because of the low luminescence efficiency of \( \text{Au}_{25}^{-}^{•} \) relative to those of \( \text{Au}_{25}^{+} \) and \( \text{Au}_{25}^{0} \) (Figure 4.7), and the quenching of the excited state mentioned above.

\[
\begin{align*}
\text{Au}_{25}^{+} + \text{TPrA}^{•} &\rightarrow \text{Au}_{25}^{0} + \text{TPrA}^{+} \quad \text{(4.7)} \\
\text{Au}_{25}^{0} + \text{TPrA}^{•} &\rightarrow \text{Au}_{25}^{-} + \text{TPrA}^{+} \quad \text{(4.8)} \\
\text{Au}_{25}^{+} + \text{TPrA}^{•} &\rightarrow \text{Au}_{25}^{2-} + \text{TPrA}^{+} \quad \text{(4.9)} \\
\text{Au}_{25}^{0} + \text{TPrA}^{•} &\rightarrow \text{Au}_{25}^{-} + \text{TPrA}^{+} \quad \text{(4.10)} \\
\text{Au}_{25}^{2-} + \text{Au}_{25}^{0} &\rightarrow \text{Au}_{25}^{-} + \text{Au}_{25}^{-} \quad \text{(4.11)} \\
\text{Au}_{25}^{-} &\rightarrow \text{Au}_{25}^{-} + h\nu_3 \quad \text{(412)}
\end{align*}
\]

When 200 mM TPrA was added to the system, the spooling ECL spectra showed the same unique peak wavelength at 945 nm and further reduced ECL intensity relative to that with 100 mM TPrA (Figure 4.9).
Figure 4.9 Spooling ECL spectra of \( \text{Au}_{25}(\text{S(CH}_2\text{Ph})_{18}. \text{C}_6\text{F}_5\text{CO}_2 \) in the presence of 200 mM TPrA. Insets are stacked spectra and ECL-voltage curve measured by the PMT.

The \( \text{Au}_{25}^{+} \) cluster solution with TPrA concentrations of 6.3, 12.5 and 25 mM displayed a gradual increase in ECL intensity, which can be clearly seen from the corresponding accumulated ECL spectra recorded during 2 cycles of potential scanning, Figure 4.9. The same peak wavelength at 875 nm as that with 50 mM TPrA was observed in the ECL evolution and devolution processes, featuring emissions from \( \text{Au}_{25}^{0*} \) and \( \text{Au}_{25}^{+*} \) (see Figure 4.10, 4.11, 4.12).

Figure 4.10 Spooling ECL spectra of \( \text{Au}_{25}(\text{S(CH}_2\text{Ph})_{18}. \text{C}_6\text{F}_5\text{CO}_2 \) in the presence of 6.3 mM TPrA. Insets are stacked spectra and ECL-voltage curve measured by the PMT.
Figure 4.11 Spooling ECL spectra of Au$_{25}$(S(CH$_2$)$_2$Ph)$_{18}$C$_6$F$_5$CO$_2$ in the presence of 12.5 mM TPrA. Insets are stacked spectra and ECL-voltage curve measured by the PMT.

Figure 4.12 Spooling ECL spectra of Au$_{25}$(S(CH$_2$)$_2$Ph)$_{18}$C$_6$F$_5$CO$_2$ in the presence of 25 mM TPrA. Insets are stacked spectra and ECL-voltage curve measured by the PMT.

The accumulated ECL spectra revealed the same changing pattern of the ECL peak wavelength vs. TPrA concentration as in the spooling ECL spectroscopy: ECL is attributed to the Au$_{25}^+$* and Au$_{25}^0$* in the presence of [TPrA] less than 50 mM, while the light emission is mainly from Au$_{25}^-$* upon further increase in [TPrA].
Figure 4.13 Accumulated ECL spectra of 0.1 mM Au$_{25}^+$ in 1:1 acetonitrile: benzene mixture containing 0.1 M TBAP and (a) 6.3, (b) 12.5, (c) 25, (d) 50, (e) 100, and (f) 200 mM TPrA. The spectra obtained by cycling potential between -0.545 and 1.145 V.

The relative ECL quantum yield ($\Phi$) was calculated for each TPrA concentration in reference to that of Ru(bpy)$_3^{2+}$/TPrA system (see Table 4-1).
Table 4-1 Relative ECL % for Au$_{25}^+$/TPrA system with various TPrA concentrations.

<table>
<thead>
<tr>
<th>[TPrA]/mM</th>
<th>Eff. by camera %</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3</td>
<td>9.6</td>
</tr>
<tr>
<td>12.5</td>
<td>20</td>
</tr>
<tr>
<td>25.0</td>
<td>116</td>
</tr>
<tr>
<td>50.0</td>
<td>88</td>
</tr>
<tr>
<td>100.0</td>
<td>544</td>
</tr>
<tr>
<td>200.0</td>
<td>735</td>
</tr>
</tbody>
</table>

For example, in the presence of 25 mM TPrA a relative efficiency as high as 116% was reached. Please also note that with high [TPrA], the ECL quenching in the Ru(bpy)$_3^{2+}$/TPrA co-reactant system is more dramatic than that in the Au$_{25}^+$/TPrA one.$^{14}$ That is the reason why the relative efficiency in Table 4-1 shows a very high efficiency with [TPrA] larger than 100 mM.

4.4 Conclusions

NIR ECL in the Au$_{25}^+$/TPrA co-reactant system was found to be stronger than that of the Au$_{25}^+$/BPO system. The spooling ECL spectroscopy of the Au$_{25}^+$/TPrA co-reactant system was able to unambiguously discriminate three excited states, Au$_{25}^{0*}$, Au$_{25}^{+*}$ and Au$_{25}^{-*}$, and elucidate the corresponding generation mechanisms by means ECL peak wavelengths and intensity. It was discovered that TPrA concentration played a very important role in electrogenerated light emissions from the three species. It is plausible that NIR-ECL of Au$_{25}^+$ clusters can be tuned by varying the TPrA concentration and applied potential. All these will be helpful for the ECL community and molecular electrochemists in general.
4.5 References


Chapter 5

5 Thermodynamic and Kinetic Origins of Au$_{25}^0$ Nanocluster Electrochemiluminescence

- This Chapter has been published as a full paper. The corresponding reference is: Mahdi Hesari, Mark S. Workentin, and Zhifeng Ding, *Chemistry European Journal*, 2014, Accepted Aug. 18, 2014.
5.1 Introduction

Photoelectrochemistry is the study of conversions between electrons and photons in chemical processes, which is essential in electrogenerated chemiluminescence (ECL)\(^1\)\(^-\)\(^6\) and solar fuels.\(^7\)\(^-\)\(^8\) Metal clusters and polynuclear complexes are ubiquitous materials playing important roles in the above photoelectrochemistry.\(^7\)\(^,\)\(^9\)\(^-\)\(^15\) Recently, organothiolate protected \(\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}\) (\(\text{Au}_{25}^0\), \(\text{SCH}_2\text{CH}_2\text{Ph}=2\)-phenylethanolthiol) clusters along with their analogues\(^16\)\(^-\)\(^17\) have been a particular research focus due to their molecule-like (1.1 nm in diameter) structure, unique catalytic,\(^18\) optical,\(^10\)\(^,\)\(^19\)\(^-\)\(^21\) and electrochemical\(^22\)\(^-\)\(^23\) properties. It is evident that \(\text{Au}_{25}\) clusters and their excited states should have even richer photoelectrochemical properties than the classical polynuclear complexes due to their well defined redox behaviors.\(^7\)\(^,\)\(^9\) Despite this, investigation on ECL of \(\text{Au}_{25}\) clusters is scarce.\(^24\)\(^-\)\(^26\) Recently, we reported that the \(\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}^+\) cluster (\(\text{Au}_{25}^+\)) is a NIR-ECL emitter in the presence of benzoyl peroxide (BPO) as a coreactant, though the reaction process is not energetically favorable due to the multi-step reduction reaction requirement\(^24\) that causes a dramatic decrease in the emission efficiency.\(^24\) We also showed that the negatively charged \(\text{Au}_{25}\) cluster, \(\text{Au}_{25}^-\) (\(\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}^-\)), to be an effective ECL system with BPO, however ECL quenching was also observed with different BPO concentrations.\(^27\) The same charged derivatives \(\text{Au}_{25}^z\) (\(z=1\)- and \(1\)+) were employed in the presence of tri-\(n\)-propylamine (TPrA)\(^28\)\(^-\)\(^29\) as another coreactant, which generated TPrA\(^+\) intermediates upon electrochemical oxidation, to react with several of the oxidation states of the \(\text{Au}_{25}\) cluster.\(^27\)\(^,\)\(^30\) The \(\text{Au}_{25}^+\) cluster reacted with the TPrA\(^+\) and the \(\text{Au}_{25}^0\) was formed in an energetically efficient route, although higher concentration of TPrA led to the formation of other charge species such as the \(\text{Au}_{25}^-\) as the emitters. Similar to the \(\text{Au}_{25}^+/\text{BPO}\) system the \(\text{Au}_{25}^-/\text{TPrA}\) system is less efficient, due to the fact that the \(\text{Au}_{25}^-\) is required to be electrochemically oxidized in several steps to form the \(\text{Au}_{25}^+\) for further reaction with the electrogenerated TPrA\(^+\). The \(\text{Au}_{25}^0\) cluster is more readily converted to other oxidation states and herein we report our exploration on its ECL generation with the TPrA coreactant. Guidelines based on its thermodynamics and kinetic characteristics of the system will allow one to tune and control the ECL of \(\text{Au}_{25}\) clusters.
5.2 Experimental

5.2.1 Chemicals

Tetrachloroaurate (III) trihydrate, sodium borohydride, ethanol, dichloromethane, tri-\textit{n}-propylamine, benzoyl peroxide, dry acetonitrile and dry benzene were purchased from Aldrich. Tetrahydrofuran was provided from Caledon. Ethanol was supplied by Commercial Alcohol. Tetra-\textit{n}-butylammonium perchlorate (TBAP) electrolyte was bought from Fluka.

5.2.2 Instrumentation for Synthesis Characterization

UV-visible spectra were measured using a Varian Cary 5000 spectrophotometer.$^1$H NMR spectrum were recorded on a Mercury and Inova 400 spectrometers (1H: 400 MHz) in CD$_2$Cl$_2$. An AB Applied Biosystem mass spectrometer (4700 Proteomics Analyzer) was employed to obtain MALDI-TOF spectra. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) was utilized as MALDI matrix. MALDI samples were prepared by mixing 0.2:1000 analyte: DCTB, 7 µL of which was casted on the target plate and air-dried for further measurement.

5.2.3 Synthesis of Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$$^0$

HAuCl$_4$.3H$_2$O, 1.02 g, was dissolved in 100 mL tetrahydrofuran in a tri-neck rounded flask. The solution was cooled using an ice-bath and 2.1 mL 2-phenylethanethiol was added to the solution under slow stirring. The yellowish solution was turned to colorless within next 45 minutes. At this point, 998 mg NaBH$_4$ dissolved in 20 mL ice-cold water was added to the mixture all at once under vigorous stirring. A dark solution was formed upon the addition of this reducing agent, an indication of large nanoparticle formation. The mixture was stirred for 5-6 days to complete the aging step. Then, the sample was gravity filtered and an oily product was yielded after solvent volume
reduction. The excess of sodium borohydride and capping thiol was removed by washing with water/ethanol mixture. Purity of sample was examined using different techniques.

$^1$H NMR spectrum of $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}^0$ also is shown in Figure 5.1. It is worth noting that the signals at 2.8 and 5.15 ppm are an indication of the methylene groups in the 2-phenylethanethion ligands. The peak at 5.15 ppm is diagnostic for this Au$_{25}$ charge state.

![Figure 5.1](image)

**Figure 5.1** $^1$HNMR spectrum of $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}^0$, obtained in CD$_2$Cl$_2$. Residual solvent peak at 5.32 ppm.

Figure 5.2 shows Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry of $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}^0$ with DCTB as matrix with a main peak at 7394.1 Da indication of molecular mass of the $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}^0$ nanoclusters ($\text{cal.}$ 7394.1613 Da). The peak at 6051.6 indicates the most stable fragment with $\text{Au}_{21}(\text{SC}_2\text{H}_4\text{Ph})_{14}$ formula.
Figure 5.2 Matrix Assisted Laser Desorption/Ionization (MALDI) spectrum of Au$_{25}$(SC$_2$H$_4$Ph)$_{18}^0$. The stars indicate cluster fragments.

5.2.4 Spectroscopy and photoelectrochemistry

UV-visible-NIR spectrum of 0.016 mM of Au$_{25}$(SC$_2$H$_4$Ph)$_{18}^0$ was recorded using a Varian Cary 5G absorption spectrometer in the wavelength range of 300-1300 nm (4.13-0.95 eV). Figure 5.3 shows UV-Visible-NIR absorption spectrum of Au$_{25}$(SC$_2$H$_4$Ph)$_{18}^0$ nanoclusters in dichloromethane.
Figure 5.3 Absorbance-energy profile of 0.016 mM of Au$_{25}$(SC$_2$H$_4$Ph)$_{18}^0$ in dichloromethane. Inset; corresponding UV-visible-NIR absorption spectrum. The red dotted-line indicates the onset

The electrochemistry and ECL experiments were carried out in a 25 cm glass cylinder ECL cell with an inner diameter of 2.5 cm and equipped with a flat Pyrex window at the bottom for light detection. The conventional three-electrode system has been employed, with a 2 mm home-made platinum disk embedded in a glass sheath and two Pt coils serving as working, reference and counter electrodes, respectively. The ECL set-up and instrumentation details have been published elsewhere.$^{25,32-35}$ Various TPrA concentrations (6.25-200 mM) were added to the sample, while an Ar blanket was kept above the solution in the ECL cell to prevent oxygen dissolution into the solution. Since the ECL is in NIR region, ECL spectroscopy was finally conducted on an Acton 2300i spectrograph with two gratings (50 l/mm blazed at 600 nm and 300 l/mm blazed at 700 nm) and an Andor iDUS CCD camera (Model DU401-BR-DD-352) cooled at -65 °C. The wavelengths of the system were calibrated before each experiment using a Mercury-Argon lamp (Ocean Optics).
For the spooling ECL spectroscopy, the NIR set was used and the following parameters were used for the Andor Technology program under the kinetic parameters option tab: exposure time = 1 s, number of accumulations = 1, kinetic series length = xxx s to match with the potential scan time, kinetic cycle time = 1, and the spectrometer was centred at 700 nm using the 50 l/mm grating. On the CHI 610A electrochemical analyzer, the initial potential, high potential, low potential, sensitivity, initial scan polarity, scan rate, sweep segments, sample interval, and quiet time were set appropriately. Simultaneously, the CHI 610A electrochemical analyzer and the Andor Technology program were run, and the CV and spectra collected.\textsuperscript{25,36-38}

A solution of 0.1 mM Au\textsubscript{25}(SC\textsubscript{2}H\textsubscript{4}Ph)\textsubscript{18}\textsuperscript{0} in 1:1 acetonitrile: benzene contain 0.1 M tetra-\textit{n}-butylammonium perchlorate (TBAP) used to obtained cyclic voltammograms at 0.1 Vs\textsuperscript{-1}, and differential pulse voltammograms with following set up; Amplitude 0.05 V, Pulse Width 0.05 V, Sampling Width 0.02 sec, and Pulse Period 0.2 sec. Formal potentials were calculated using DPVs (Figure 5.4B), using eq. 5.1:\textsuperscript{39}

\[ E'' = E_{\text{peak}} + \frac{\Delta E}{2} \quad (5.1) \]

Before running ECL experiments at each TPrA concentration, the two quasi-reversible redox waves of the Au\textsubscript{25} in the middle of potential window (E\textsubscript{30}' = 0.320 and E\textsubscript{20}' = -0.060 V vs. SCE) were identified as an internal standard to calibrate the potential window (Figure 5.4). Then, ferrocene was added to the solution to verify the above potential calibration after ECL experiments, taking its formal redox potential, E\textsuperscript{°} (Fc/Fc\textsuperscript{+}), as 0.424 V vs. SCE in 1:1 acetonitrile: benzene.\textsuperscript{40}

ECL efficiency was determined by integrating ECL-voltage curves and comparing the integrated ECL intensities and the charge of the analyte in reference to those of Ru(bpy)\textsubscript{3}\textsuperscript{2+}, using the below equation:

\[ \Phi_x = 100 \frac{\int_a^b \text{ECL} \ dt}{\int_a^b \text{Current} \ dt} \frac{\int_a^b \text{ECL} \ dt}{\int_a^b \text{Current} \ dt} \]

where \( \Phi \) is the quantum yield (%) relative to Ru(bpy)\textsubscript{3}\textsuperscript{2+}, ECL is the ECL intensity, Current the electrochemical current value, St is the Ru(bpy)\textsubscript{3}\textsuperscript{2+} and x is the sample.
The photoluminescence spectrum of each pure Au$_{25}$ cluster charge state was obtained with its 0.1 mL solution in 1:1 acetonitrile: benzene mixture and a 532 nm laser was used to excite the sample. The spectra were acquired using the Andor BRDD CCD camera cooled at -65 °C, to exclude any ambiguities about the PL spectrum of the clusters measured on different instruments/detectors. ECL peak wavelengths are usually a few nanometers red-shifted relative to those of PL due to self-absorption or inner filter effect.

Calculation of quantum yields of Au$_{25}$(SR)$_{18}^z$ PL; the quantum yield ($\Phi$) of the Au$_{25}$(SR)$_{18}^z$ ($z=1^-, 0$ and 1+) PL was found by comparing the photoluminescence intensities values of the Au$_{25}$ samples with the references Ru(bpy)$_3^{3+}$.

### Table 5-1 Integrated PL efficiency of Au$_{25}^z$ ($z =1^+, 0$ and 1-) versus Ru(bpy)$_3^{2+}$.

<table>
<thead>
<tr>
<th>Au$_{25}$(SC$_2$H$<em>4$Ph)$</em>{18}^z$</th>
<th>PL Eff. vs. Ru(bpy)$_3^{2+}$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$z =1^+$</td>
<td>14.8</td>
</tr>
<tr>
<td>$z =0$</td>
<td>0.7</td>
</tr>
<tr>
<td>$z =1^-$</td>
<td>0.55</td>
</tr>
</tbody>
</table>

### 5.3 Results and Discussion

#### 5.3.1 Electrochemistry of Au$_{25}^0$ nanoclusters

Figure 5.4A shows the cyclic voltammogram (CV) of 0.1 mM Au$_{25}^0$ clusters in 1:1 benzene: acetonitrile containing 0.1 M tetra-$n$-butylammonium perchlorate (TBAP) as the supporting electrolyte. On scanning the applied potential from 0.05 V (labeled with a cross. +) vs. SCE toward more negative potentials, the Au$_{25}^0$ gains one electron quasi-reversibly and forms the Au$_{25}^-$ at a formal potential of -0.06 V ($E_1^{°}$), which is further reduced at -1.68 V ($E_2^{°}$) to form first the Au$_{25}^{2-}$, and possibly more highly reduced...
forms. The formal potentials were more easily determined from differential pulse voltammograms (DPVs) demonstrated in Figure 5.4B. Notice that the difference between $E_1^{\circ}$ and $E_2^{\circ}$ (-1.61 V), correcting for the charging energy of 0.29 V from the spacing between the formal potentials of the Au$_{25}^{0/1^-}$ and Au$_{25}^{1+/0}$ waves, represents the HOMO-LUMO electrochemical energy gap, 1.32 eV. Upon scanning the potential to positive values from the starting potential, the Au$_{25}^0$ losses one electron and forms the Au$_{25}^+$ at 0.19 V ($E_3^{\circ}$) quasi-reversibly, which is further oxidized at 0.84 V ($E_4^{\circ}$) to form the Au$_{25}^{2+}$. The redox reaction wave pattern is very similar to those in CH$_2$Cl$_2$ and toluene/acetonitrile. The above formal potential values agree qualitatively with those determined from similar Au$_{25}^-$, Au$_{25}^+$ clusters in CH$_2$Cl$_2$ and Au$_{25}^+$ clusters in 1:1 acetonitrile: benzene solutions. The $E_1^{\circ}$ and $E_3^{\circ}$ values agree very well with those reported.
Figure 5.4 (A) Cyclic voltammogram at scan rate of 100 mVs\(^{-1}\) and (B) differential pulse voltammograms of the 0.1 mM Au\(_{25}^0\) in 0.1 M TBAP 1:1 benzene: acetonitrile electrolyte solution. The dashed curves indicate background currents.

Figure 5.5 displays the PL spectra of independently synthesized Au\(_{25}^-\), Au\(_{25}^0\) and Au\(_{25}^+\) clusters in 1:1 acetonitrile: benzene, each at a concentration of 0.1 mM, which are similar to those used for the Au\(_{25}^-\) study by the Jin\(^{11,33}\) and Murray\(^{35}\) groups, and to the Au cluster investigated by El-Sayed and Whetten.\(^{36}\) Further details on the origin of
photoluminescence emissions of $\text{Au}_{25}^0$ and $\text{Au}_{25}^-$ nanoclusters were reported by Green et al.\textsuperscript{37} They used femtosecond time-resolved spectroscopy along with a fitting model.

![Photoluminescence spectra of $\text{Au}_{25}^+$ (dotted-line), $\text{Au}_{25}^0$ (dashed-line), and $\text{Au}_{25}^-$ (solid-line) in 1:1 acetonitrile: benzene mixture.](image)

**Figure 5.5** Photoluminescence spectra of $\text{Au}_{25}^+$ (dotted-line), $\text{Au}_{25}^0$ (dashed-line), and $\text{Au}_{25}^-$ (solid-line) in 1:1 acetonitrile: benzene mixture.

Notably, the main dominant peak wavelengths in Figure 5.5 were assigned to relaxing excited states across the HOMO-LUMO gaps are 860 nm (1.44 eV), 865 (1.43 eV), and 945 (1.31 eV) nm for the clusters with charges +1, 0 and -1, respectively. The shoulders before and after these peak wavelengths in the PL spectra might be the excited states populated from the electron promotion from HOMO-1 to LUMO or HOMO to LUMO+1, as well as the semi-ring states.\textsuperscript{20, 22, 36-37} It is plausible that the $\text{Au}_{25}^-*$ can be identified by the longer wavelength, while the $\text{Au}_{25}^+*$ can be distinguished from the other two excited states by its higher emission intensity than the others due to its higher
probability of electron relaxation. While the potentials of the redox processes in Figure 5.4 provide the basis for the bottom line of the Latimer-type diagram in Figure 5.6, the energy levels of the excited species in the diagram are now completed by connecting vertically to their corresponding ground states. Thermodynamically, the six reduction potentials involving the $\text{Au}_{25}^{2+/0*}$, $\text{Au}_{25}^{+0*/0}$, $\text{Au}_{25}^{0/-*}$, $\text{Au}_{25}^{-*/2-}$, $\text{Au}_{25}^{0/*-2}$, and $\text{Au}_{25}^{+0*/0}$ in the Latimer-type diagram (Figure 5.6) were calculated from the results of the above spectroscopic and electrochemical data, as has been done for other polynuclear complexes.7, 9, 38

**Figure 5.6** Latimer-type diagram showing the relationship of redox potentials of $\text{Au}_{25}$ cluster ground and excited states.

The most comprehensive Latimer-type diagram for the clusters to date in Figure 5.6 reveals an extremely rich electrochemistry of the $\text{Au}_{25}$ clusters including their several excited species, which leads to a grand avenue toward exploring potential ECL generation of the cluster. Due to the instability and/or slow reactivity of the electrogenerated $\text{Au}_{25}$ species, $\text{Au}_{25}^{2+}$ and $\text{Au}_{25}^{2-}$, no ECL emission via annihilation from the $\text{Au}_{25}^{0}$ solution was observed, which is similar to the observation on the annihilation ECL process in the $\text{Au}_{25}^{−}$ solution.27

Therefore, we employed TPrA as a coreactant that generates the TPrA$^*$ upon oxidation as a highly reducing intermediate. In fact, TPrA undergoes an irreversible oxidation, via the generation of TPrA$^{+*}$, which readily loses $\text{H}^+$ and produces highly reductive TPrA$^*$ ($E°' = -1.70 \text{ V vs. SCE}$29). No ECL was observed during the TPrA electrochemical/chemical reaction processes in the absence of the Au cluster. It is
plausible that the TPrA$^-$ will be able to react with the \( \text{Au}_{25}^{2+} \), \( \text{Au}_{25}^+ \) and \( \text{Au}_{25}^0 \), leading to emissive species \( \text{Au}_{25}^{+*} \), \( \text{Au}_{25}^{0*} \) and \( \text{Au}_{25}^{-*} \), respectively (Figure 5.6).

5.3.2 ECL study of \( \text{Au}_{25}^0 \) nanoclusters in the presence of TPrA

The ECL spectroscopy of the \( \text{Au}_{25}^0 \) nanocluster was investigated with various TPrA coreactant concentrations of 6.3, 12.5, 25.0, 50.0, 100, and 200 mM in order to gain insight into the \( \text{Au}_{25}^0 \) ECL mechanisms and tune the excited states. Figure 5.7A displays the recorded ECL spectra acquired on an Andor BR-DD CCD camera attached to an Acton spectrograph along with the corresponding potential (spooling) for 0.1 mM \( \text{Au}_{25}^0 \) solution with 12.5 mM TPrA during potential scanning between 0.025 and 1.235 V. The onset of the ECL is at 0.725 V vs. SCE, at which potential the electrogenerated \( \text{Au}_{25}^+ \) and TPrA$^-$ (Figure 5.4B) interacted in the vicinity of the electrode. As shown in Scheme 5.1, the \( \text{Au}_{25}^+ \) gained one electron in its LUMO orbitals via an electron transfer (ET) from low concentration of TPrA$^-$ at this potential and formed \( \text{Au}_{25}^{0*} \) excited state that emitted light at a peak wavelength of 880 nm, 1.41 eV (left inset of Figure 5.7A). This emission wavelength is in agreement with that of recorded PL spectrum (865 nm) of the pure \( \text{Au}_{25}^0 \) (Figure 5.5C, the dashed-line curve). Upon scanning the potential more positive, the \( \text{Au}_{25}^+ \) undergoes further oxidation at 0.840 V vs. SCE, producing the highly reactive \( \text{Au}_{25}^{2+} \) (Figure 5.4B). ECL intensity in the potential range of 0.825 to 1.125 V increased dramatically. Similar to Scheme 5.1, TPrA$^-$ in this case reacted with \( \text{Au}_{25}^{2+} \) to generate \( \text{Au}_{25}^{+*} \) (Scheme 5.2), which emitted more intense light than \( \text{Au}_{25}^{0*} \) at the same wavelength of 880 nm. The above observation agrees with that on the PL spectra: emission intensity increased while the peak wavelength at 880 nm changes very little. The ECL spectrum shows a further increased intensity and reaches a maximum at 1.125 V corresponding to \( \text{Au}_{25}^{+*} \). The ECL emission decreased when the applied potential continued to be increased to more positive potentials due to depletion in the TPrA$^-$ concentration.
Figure 5.7 Spooling ECL spectra of 0.1 mM Au$_{25}^0$ in the presence of (A) 12.5 mM (B) 50.0 mM and (C) 200.0 mM of TPrA in 1:1 benzene: acetonitrile mixture containing 0.1 M TBAP as the support electrolyte. The applied potentials are labeled for each spectrum. The insets show the ECL evolution and devolution in a format better clarifying the wavelengths of the ECL emission.
The correlated light emission vs. potential plot (ECL-voltage curve) of the system is shown in Figure 5.8, which shows the same variation as that observed for the spooling ECL spectra in Figure 5.7A.

**Figure 5.8** Cyclic voltammogram and ECL-voltage curve of 0.1 mM Au$_{25}^0$ in the presence of 12.5 mM TPrA in 1:1 acetonitrile: benzene solvent mixture, containing 0.1 M TBAP, with a scan rate of 0.1 Vs$^{-1}$.

**Scheme 5.1** Proposed mechanism in the potential window from 0.025 to 0.725 V.
Further elucidation of the excited states was carried out using improved \textit{in-situ} spectrophotoelectrochemistry. \textsuperscript{27, 39-40} In a typical experiment, 0.1 mM of the Au\textsubscript{25}\textsuperscript{0} solution in benzene: acetonitrile (0.1 M TBAP) solution in a 1 mm thin layer quartz cuvette was electrolyzed to a destiny oxidation state with a platinum mesh (6×7 mm) biased at a corresponding potential (see Figure 5.4A), while PL spectra with an excitation laser wavelength of 532 nm were recorded on the same CCD camera and spectrograph set at a time interval of 2 s. Figure 5.9 illustrates the \textit{in-situ} spectrophotoelectrochemistry set-up.
Figure 5.9 Schematic illustration of in-situ spectrophotoelectrochemical set-up.

Figure 5.10 demonstrates the in-situ PL spectra of the Au$_{25}^{2+}$, Au$_{25}^+$, Au$_{25}^0$, Au$_{25}^-$ and Au$_{25}^{2-}$ (A-E). Except the Au$_{25}^0$, all the oxidation states were obtained by electrolyzing the Au$_{25}^0$ at potential values applied to the Pt mesh in the 1 mm thin layer cell (Figure 5.9). These potentials were determined from the DPVs in Figure 5.4B. As illustrated by the stack PL spectra in each course of the electrolysis, Figure S5.1, the transition from the Au$_{25}^0$ to Au$_{25}^+$ revealed an increase in PL intensity at a constant wavelength of 840 nm, Figure S5.1A, while the conversion from the Au$_{25}^0$ to Au$_{25}^-$ displayed a red shift in PL peak wavelength to 960 nm and a relative low intensity.
Figure 5.10 *In-situ* PL spectra of Au$_{25}^z$, where $z=2^+, 1^+, 0, 1^-$ and 2$^-$ (A-E), which were obtained in the course of electrolysis of a 0.1 mM Au$_{25}^0$ solution to the destiny oxidation states. The applied potentials to the Pt mesh in the 1 mm thin layer cell were determined from DPVs in Figure 5.4B. The excitation laser wavelength was at 532 nm. A razor edge filter was employed to separate the laser light from PL.
Needless to say, the electrogenerated $\text{Au}_{25}^0$, $\text{Au}_{25}^+$ and $\text{Au}_{25}^-$ show a similar PL spectrum pattern in Figure 5.10 as that of the three pure species in Figure 5.5. All these observations support our assignment of excited species in the ECL processes in Figure 5.7A. The ECL intensity augments with the increasing TPrA concentration ([TPrA]) in the range of 6.3 to 25.0 mM (compare Figure 5.7A with Figure 5.11A-B).

**Figure 5.11** Spooled ECL spectra of 0.1 mM $\text{Au}_{25}^0$ in the presence of (A) 6.3 mM, (B) 25.0 mM and (C) 100.0 mM of TPrA in 1:1 acetonitrile: benzene solvent mixture containing 0.1 M TBAP.
The ECL evolution and devolution follow a similar pattern as that with 12.5 mM TPrA in Figure 5.7A. It should be noticed that ECL is highly dependent on the initial [TPrA] (and ultimately the [TPrA*]. With 6.3 mM [TPrA] (Figure 5.9A), the ECL reached a maximum intensity of only 22 counts at the applied potential of 0.935 V and decayed rapidly. This is because of the low [TPrA] and corresponding low [TPrA ] which leads to depletion for the Au$_{25}^{+*}$ generation reaction (Scheme 5.2). When the initial [TPrA] was increased to 12.5 mM, ECL intensity was increased 12 times of that with 6.3 mM TPrA. When the applied potential was scanned back to 0.642 V, Figure 5.5A, the ECL intensity smoothly decreased. In the case of using 25.0 mM TPrA initial concentration, ECL was further increased 43 fold larger than that with 6.3 mM TPrA at the potential of 1.132 V and stayed in emission till the applied potential back to 0.532 V.

Interestingly, with [TPrA] of up to 50 mM, the ECL intensity increased continually until the reverse potential scanning to 0.954 V, reaching a maximum count as high as 95 times relative to that with 6.25 mM [TPrA], Figure 5.7B. At these concentrations, the [TPrA*] is in excess and reacted with bulk Au$_{25}^{0}$ to generate Au$_{25}^{-*}$, giving off an ECL onset peak at wavelength of 960 nm. In the potential range between 0.737 (ECL onset potential) and 0.837 V (before $E_4''$ for Au$_{25}^{+}$ to be oxidized to Au$_{25}^{2+}$), it is apparent that ECL generation followed a new mechanism involving Au$_{25}^{0}$ and TPrA* electron transfer as expressed by Scheme 5.3. With the applied potential further moved toward more positive potentials, Au$_{25}^{2+}$ dominated in the vicinity of the electrode and Au$_{25}^{+*}$, with high emission yield, was generated (Scheme 5.2). The ECL peak wavelength displayed a blue shift. It is worth noting that the ECL has a contribution from Au$_{25}^{-*}$ as identified by the red-shifted peak wavelength upon the potential being scanned back to 0.554 V. ECL wavelengths are facile to tune and control based on the above observations (Schemes 5.1-3).
A further increase in the [TPrA] to 100 mM (Figure 5.11C) and 200 mM (Figure 5.11C) caused the ECL evolution and devolution to display a unique peak wavelength at 960 nm, correlating to Au\(_{25}^{-}\) emission (Scheme 5.3). The high [TPrA\(^{+}\)] attributed mainly to the ECL generation via injection of an electron to Au\(_{25}^{0}\) presented in the bulk solution or electrogenerated through sequential reduction of all other Au\(_{25}\) species (Au\(_{25}^{+}\) and Au\(_{25}^{2+}\)) in the vicinity of the electrode. The alternative route of this reduction process involves injection of electron to the LUMO orbitals of Au\(_{25}\) species (Au\(_{25}^{+}\) and Au\(_{25}^{2+}\)) and the generation of the corresponding excited states (Au\(_{25}^{0*}\) and Au\(_{25}^{+*}\)) via reaction between these species and the TPrA\(^{+}\). Subsequently, Au\(_{25}^{0*}\) and Au\(_{25}^{+*}\) will relax to the ground states and eventually Au\(_{25}^{0}\) forms (Scheme 5.4).

**Scheme 5.3** Additional proposed mechanism for high [TPrA].

**Scheme 5.4** Alternative route for the reduction of Au\(_{25}^{2+}\) to Au\(_{25}^{0}\) via two-step reaction/relaxation.
Figure 5.12 shows accumulated ECL spectra recorded within the electrochemical cycling (2 cycles) between -0.30 V (starts at 0.086 V where there is no Faradic current) and 1.23 V vs. SCE with an acquisition time of 60 s. The ECL intensity reached also to the highest value at 50 mM TPrA and there was a blue shift tendency for the ECL peak wavelength in the TPrA concentration range between 6.3 and 200.0 mM. However, less information can be obtained than spooling ECL spectroscopy as described above.

**Figure 5.12** Accumulated ECL spectra of Au$_{25}^0$ in the presence of different TPrA concentrations: (A) 6.25 mM, (B) 12.5 mM, (C) 25 mM, (D) 50 mM, (E) 100 mM, and (F) 200 mM. Each spectrum obtained during two cycles (60 sec) of potential scanning between 0.04 to 1.1 and -0.3 V vs. SCE at a scan rate of 0.1Vs$^{-1}$ using the Andor BR-DD iDus camera cooled at -65 °C.
Remarkably, the ECL efficiency of the $\text{Au}_{25}^{0}/\text{TPrA}$ system reached to 103% at 25 mM TPrA relative to that of the well known $\text{Ru(bpy)}_3^{2+}/\text{TPrA}$ system (Table 5-2). ECL quenching in the $\text{Ru(bpy)}_3^{2+}/\text{TPrA}$ coreactant system is very dramatic when the [TPrA] is high.\textsuperscript{30} That is the reason why the relative efficiency in Table 5-2 probably shows overestimated efficiencies with [TPrA] larger than 100 mM.

**Table 5-2** Integrated ECL efficiency of $\text{Au}_{25}^{0}$ in the presence of various TPrA concentrations.

<table>
<thead>
<tr>
<th>TPrA concentration (mM)</th>
<th>Eff. by Camera %</th>
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<tr>
<td>6.3</td>
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<td>173</td>
</tr>
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<td>200</td>
<td>249</td>
</tr>
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</table>

### 5.4 Conclusion

The [TPrA] along with the applied potential can be used to tune the ECL wavelength and intensity based on the above thermodynamic and kinetic origins. For instance, the $\text{Au}_{25}^{0}$ cluster solution containing 50 mM TPrA emits intense light at 960 nm at the working electrode biased at 0.737 V, while the same solution emits very strongly at 880 nm if the electrode potential is held to 0.954 V. These results serve as an exciting development toward controlling ECL generation of $\text{Au}_{25}$ clusters. The ECL of $\text{Au}_{25}$ clusters was favored in the electronic relaxation across the HOMO-LUMO gap and did not depend on semi-ring state emission. The ECL intensity is superior to that of silicon
nanocrystals which relies on the presence of rich surface states,\(^1\) as previously reported by Ding et al.

5.5 References


Chapter 6

6 NIR Electrochemiluminescence from $\text{Au}_{25}^-$ Clusters Facilitated by Highly Oxidizing and Reducing Coreactant Radicals

- This Chapter has been published as a full paper. The corresponding reference is: Mahdi Hesari, Mark S. Workentin, and Zhifeng Ding, *Chemical Science*, 2014, 5, 3814-3822.

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6.1 Introduction

Electrochemiluminescence or electrogenerated chemiluminescence (ECL) \(^{1-2}\) is based on light emission from an excited state formed in the course of electron transfer processes (ET) between radical cations and anions of a luminophore, electrogenerated at a working electrode. ECL can be greatly enhanced by means of reactions of luminophore radicals with highly oxidizing or reducing radicals from co-reactants such as tri-\textit{n}-propylamine (TPrA)\(^{3-4}\) and benzoyl peroxide (BPO),\(^{5}\) produced electrochemically. ECL has found a wide range of applications such as in immunoassay\(^{6-7}\) in the presence of various water soluble co-reactants.\(^{2}\) There have been many reports on luminescent molecules emitting in the visible region, while near infrared (NIR) ECL emitters such as graphite oxide\(^{8}\) and quantum dots are scarce.\(^{9}\) NIR light at low wavelengths in the range between 700 and 2000 nm is very useful in bio-imaging techniques as it is not absorbed by cells and tissues.\(^{10}\) Gold clusters (size $<$ 2 nm) were recently introduced as ECL emitters in the visible range, from which the ECL signal was employed as an analytical probe for measuring organic and inorganic species.\(^{11-12}\) In contrast, we subsequently discovered that well-defined \(\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}^+\) (\(\text{Au}_{25}^+, \text{SC}_2\text{H}_4\text{Ph} = \text{phenylethanethiol}\)) clusters emit NIR-ECL in 1:1 acetonitrile: benzene electrolyte solution through both the annihilation and co-reactant (with BPO) routes.\(^{13}\) We elucidated ECL mechanisms, where the ECL was originated from the \(\text{Au}_{25}^+\) emitting in NIR region upon relaxation to its ground state. We suggest that the NIR ECL was probably from the electron transition across the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) mainly contributed from the \(\text{Au}_{13}\) core in the \(\text{Au}_{25}^+\). The intensity of the emitted light during annihilation was found to be very weak, likely due to the very short lifetime and slow reactivity of the reactive \(\text{Au}_{25}^{2-}/\text{Au}_{25}^+\) species generated electrochemically. Subsequently, BPO was utilized to enhance the ECL intensity. Both the \(\text{Au}_{25}^+\) and BPO were electrochemically reduced to form the \(\text{Au}_{25}^{2-}\) and highly oxidizing benzoate radical that further reacted to generate the emissive \(\text{Au}_{25}^{2-}\).
Herein, we report our discovery on the ECL mechanisms of the more stable $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}^-$ (abbreviate as $\text{Au}_{25}^-$) in the presence of both TPrA and BPO as co-reactants, from which electrogenerated radicals possessing high reducing ($E^\circ_{\text{TPrA}^*} = -1.7 \text{ V vs. SCE}$) and oxidizing ($E^\circ_{\text{benzoate}^*} = +1.5 \text{ V vs. SCE}$) power were generated, respectively. The $\text{Au}_{25}^-$ is relatively easy to prepare and the crystal structure is known. This Au cluster is also well-established for many applications such as in catalysis. Importantly, it shows rich and well-defined electrochemical and optical features that provide the necessary information allowing one to more easily understand the electronic structure, necessary for fundamental studies including ECL. Given the easily accessible redox states [$\text{Au}_{25}^q (q=2^-, 1^-, 0, 1^+, 2^+)$] from this stable $\text{Au}_{25}^-$ precursor, which can be easily electrogenerated in the vicinity of electrode, there are a number of plausible electron transfer processes between them and either the TPrA$^*$ or the benzoate radical electrogenerated from the corresponding co-reactant. As a result, a wide-range of excitation states are expected to be accessible. We elucidate the electrogenerated-excited states emitting at 950 and 890 nm in the NIR region. The states responsible for these NIR emissions were confirmed by comparison of the ECL to the photoluminescence spectra of the in-situ generated three $\text{Au}_{25}$ clusters, $\text{Au}_{25}^q (q=1^-, 0$ and $1^+)$). The ECL mechanisms/states were assigned using our spooling ECL spectroscopy, which gave insight into controlling ECL emissions in the wavelength and intensity by means of the applied potential and co-reactant concentrations. These fundamental ECL studies of Au clusters, in this case the $\text{Au}_{25}$, are beneficial for further understanding their electronic structures and are anticipated to lead to electroanalytical detections or bio-imaging.

6.2 Experimental

6.2.1 Chemicals

Tetrachloroaurate trihydrate, tetra-$n$-octylammonium bromide, tetrahydrofuran, phenylethane thiol, sodium borohydride, tri-$n$-propyl amine, benzoyl peroxide, dry
acetonitrile, dry benzene, tera-\textit{n}-butylammonium perchlorate and deuterated dichloromethane were purchased from Aldrich. Ethanol (95\%) was obtained from Commercial Alcohol Inc.

6.2.2\text{ Au}_{25}^-\text{ cluster synthesis}

\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}\text{TOA (Au}_{25}^-) was synthesized following the established protocol.\textsuperscript{16} Briefly 1.05 g (2.66 mmol) \text{Au}^{3+} salt and 1.66 g (1.2 eq.) were co-dissolved in 100 mL THF. The dark–red solution was cold to 0\textdegree C and then 6 eq. thiol was added to the mixture. After 2 hours, a colorless mixture was obtained, indication of -(\text{Au-S-Au-S})- polymer formation. At this point, 10 eq. of sodium borohydride was dissolved in 20 mL MilliQ water and added to the mixture while stirring vigorously. The mixture was left to react for 5 days and then gravity filtered to separate away the side product(s). The purification consisted of washing repeatedly with ethanol/water mixture to obtain brown solid. The pure \text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}.\text{TOA was extracted from the solid using acetonitrile. The cluster was crystallized and then the sample purity as verified using UV-Vis-NIR spectroscopy (Figure 6.1), indicating three main peaks at 400, 420 and 680 nm.}

6.2.3\text{ Characterization}

The UV-Vis-NIR spectroscopy was carried out using Cary 5G spectrometer in 1:1 acetonitrile: benzene mixture. $^1$HNMR spectra were recorded on a Varian Mercury 400 MHz in CD$_2$Cl$_2$. Photoluminescence (PL) spectra were measured on an Acton spectrograph equipped with an Andor BR-DD CCD camera that was cooled to -65 °C prior to the experiments. An AB Applied Biosystem mass spectrometer (4700 Proteomics Analyzer) was employed to obtain the MALDI-TOF spectra. The sample was prepared by mixing a 0.2:1000 analyte: matrix ratio. Then, 7 $\mu$L of the mixture was cast on the target plate and air-dried. A MicrOTOF (Bruker) mass spectrometer was used to record ESI mass spectra of \text{Au}_{25}^- in CH$_2$Cl$_2$-methanol solvent mixture.
Figure 6.1 UV-Vis-NIR spectrum (in the energy scale) of the Au$_{25}^-$ in dichloromethane. The inset shows the same spectrum in the wavelength scale.

Figure 6.2 shows $^1$H NMR spectrum of the synthesized and crystallized Au$_{25}$(SC$_2$H$_4$Ph)$_{18}$TOA obtained in CD$_2$Cl$_2$. The spectrum shows peaks corresponding to the presence of tetra-$n$-octylammonium at 0.9 ppm (terminal –CH$_3$), high multiplicity in the range of 1.18–1.9 ppm related to methylene groups and a triplet at 3.3 ppm for the $\alpha$-methylene in -N$^+$-CH$_2$-CH$_2$-.$^{13}$
Figure 6.2 $^1$H NMR spectrum of the crystallized Au$_{25}^-$ in $d_2$-dichloromethane. Residual solvent peak at 5.32 ppm.

Further analysis of the clusters was performed using electrospray ionization (ESI) mass spectrometry as shown in Figure 6.3. The theoretical molecular mass of Au$_{25}$(SC$_2$H$_4$Ph)$_{18}$ is 7394.85 Da, while experimentally a peak with 7393.8 was observed. The corresponding molecular mass region is expanded and shown as the inset of Figure 6.3. This evidence supports the synthesized and purity of the negatively charged Au$_{25}$ clusters that used in the electrogenerated chemiluminescence studies.
Figure 6.3 Electrospray ionization (ESI) mass spectrum of the Au_{25}(SC_{2}H_{4}Ph)_{18}.TOA, obtained in CH_{2}Cl_{2}/Methanol mixture.

6.2.4 Electrochemistry, ECL and spectrophotoelectrochemistry

The electrochemical and electrochemiluminescence experiments were performed in a glass cylinder (20 cm in length and 15 mm in diameter) with a flat Pyrex window at the bottom for light detection. The above ECL cell was placed on top of a photomultiplier tube or spectrograph and camera set to record ECL-voltage curves and accumulated/spooling ECL spectra, respectively. The wavelength was calibrated prior to each experiment using a Mercury lamp.

A solution of the Au_{25}− (0.1 mM) was prepared in a glovebox (N_{2} atmosphere) using dry 1:1 acetonitrile: benzene mixture. After studying the electrochemistry of the sample various concentrations of TPrA, namely 6.3, 12.5, 25, 50, 100, and 200 mM were added to the solution under Ar atmosphere. A 2 mm diameter Pt disc embedded in glass and two Pt wires served as working, reference and counter electrodes, respectively. All the potentials were calibrated against the Fc/Fc^{+} redox couple with respect to the saturated calomel electrode (SCE) (E_{Fc/Fc^{+}} = 0.424 V vs. SCE). Further details about the ECL set up can be found in ref. 13.
The PL spectra of various Au$_{25}$ charge states were obtained by electrolysis at the appropriate potentials (vide infra) of a 0.1 mM Au$_{25}^-$ electrolyte solution, freshly prepared under Ar atmosphere in a 1 mm thin layer quartz cell (BASi). The electrolysis was performed using a Pt mesh as the working electrode, a Ag wire immersed in 0.01 M Ag$^+$/0.1 M TBAP in acetonitrile as the nonaqueous reference electrode, and a Pt wire as the counter electrodes.\textsuperscript{19} A 532 nm laser was utilized to irradiate the mesh electrode area, where the various charged Au$_{25}$ species were electrochemically produced \textit{in-situ}, while the PL signal was acquired from the narrow side of the thin layer solution by means of the same CCD camera and Acton spectrograph set. A long-pass edge filter was placed between the sample and the spectrograph entrance to cut the excitation wavelength and harmonic peaks. For instance, PL spectra of the Au$_{25}^0$ and Au$_{25}^+$ were obtained via \textit{in-situ} PL acquisition of electrolyzed solution biased at 0.05 and 0.32 V \textit{vs.} SCE, respectively.

6.3 Results and Discussion

6.3.1 Electrochemistry, spectroscopy and ECL in the annihilation route

Figure 6.4 illustrates differential pulse voltammograms (DPVs) of 0.1 mM Au$_{25}^-$ clusters in 1:1 acetonitrile: benzene mixture containing 0.1 M tetra-$n$-butylammonium perchlorate (TBAP) as the supporting electrolyte. The electrochemical investigation on this cluster matched those reported by the Murray and Jin groups.\textsuperscript{20-21}
Figure 6.4 Differential pulse voltammetry of 0.1 mM Au$_{25}^-$ in 1:1 acetonitrile: benzene containing 0.1 M TBAP. Scan rate was at 100 mVs$^{-1}$. Arrows in the figure show potential scan directions.

Briefly, in the potential range between -1.90 and 1.10 V, four redox waves with formal potentials of -1.640, 0.038, 0.280 and 0.949 V vs. SCE can be observed, corresponding to electrochemical reactions of Au$_{25}^{2-}$/Au$_{25}^-$, Au$_{25}^-$/Au$_{25}^{0}$, Au$_{25}^{0}$/Au$_{25}^+$ and Au$_{25}^+$/Au$_{25}^{2+}$ redox couples, respectively. The anodic (black) and reversed cathodic (red) potential scan demonstrate the quasi-reversible nature for the conversion between the Au$_{25}^-$ and Au$_{25}^{0}$, and for that between the Au$_{25}^{0}$ and Au$_{25}^+$. The Au$_{25}^{2-}$ and Au$_{25}^{2+}$ are not stable as illustrate by the decreased anodic and cathodic peak heights relative to their counterparts, respectively. The HOMO-LUMO energy gap, determined from the first oxidation and reduction peak potential difference after the charge correction, is 1.33 eV which is in close agreement with the reported value. Similar energy gap value ca. 1.36 eV can also be calculated from the onset of UV-Vis-NIR absorption spectrum (Figure 6.1). The above physicochemical properties along with the crystal structure of the Au$_{25}$(SC$_2$H$_4$Ph)$_{18}$TOA$^{23-24}$ and calculated electronic structure as well as their correlations to the UV-Vis-NIR$^{24}$ and PL data,$^{25-26}$ particularly those obtained from the PL spectra of the different charges$^{19}$ give a roadmap of photoelectrochemistry for the Au$_{25}^-$ cluster.
ECL of the Au$_{25}^-$ cluster was then investigated. In a typical annihilation ECL experiment, 0.1 mM Au$_{25}^-$ in 1:1 acetonitrile: benzene electrolyte was used, where the applied potential at the working electrode was swept between -1.8 and 1.2 V vs. SCE. As depicted by the ECL-voltage curve in Figure 6.5, no appreciable ECL was observed.

![ECL-Voltage curve and cyclic voltammogram of 0.1 mM Au$_{25}^-$ in in 1:1 acetonitrile:benzene containing 0.1 M TBAP. Scan rate was at 100 mVs$^{-1}$. The arrow indicates the starting potential.](image)

**Figure 6.5** ECL-Voltage curve and cyclic voltammogram of 0.1 mM Au$_{25}^-$ in in 1:1 acetonitrile:benzene containing 0.1 M TBAP. Scan rate was at 100 mVs$^{-1}$. The arrow indicates the starting potential.

This is most likely due to the low reaction rate of the two cluster cores and the short lifetime$^{27}$ of the electrogenerated reactive intermediates Au$_{25}^{2-}$ and Au$_{25}^{2+}$ that did not permit a significant concentration of both species to react for any ECL generation. The low stability of the two radicals can be surmised from the irreversibility of the two reactions on the most right and left positions in the DPVs at a slow scan rate in Figure 6.4.
6.3.2 ECL of the Au$_{25}^-$ in the presence of TPrA

Notably, the addition of a co-reactant such as TPrA could greatly enhance the ECL intensity. TPrA is suitable for our study due to the rich electrochemistry of the Au$_{25}^-$ in the anodic region (Figure 6.4). TPrA undergoes an oxidative process, forms the corresponding TPrA radical cation that then deprotonates rapidly to generate the highly reducing TPrA$^+$ ($E^\circ = -1.7$ V vs. SCE) (eqs. 6.1 and 6.2). This provides an appropriately high concentration of a highly reducing species in solution to react with the short-lived oxidized form of the Au$_{25}^-$. To this end, various TPrA concentrations, ranging from 6.3, 12.5, 25, 50, 100, to 200 mM were added for the ECL enhancement in the 0.1 mM Au$_{25}^-$ solution. Figure 6.6 demonstrates the results from a typical experiment where 12.5 mM TPrA was added to a 0.1 mM solution of the Au$_{25}^-$. 

![Figure 6.6](image)

**Figure 6.6** Spooling ECL spectra of 0.1 mM Au$_{25}^-$ in the presence of 12.5 mM TPrA in 1:1 acetonitrile: benzene containing 0.1 M TBAP during the potential scan from -0.33 V to 1.33 V and back to -0.33 V at a scan rate of 100 mVs$^{-1}$ (A) along with the cyclic voltammogram (B). An Andor BR-DD CCD camera (cooled at -65°C) was used to acquire the spectra at a time interval of 1 s or potential interval of 100 mV. Insets represent stack spectra of spooling for clarity of the corresponding wavelength, where the same color-coded PL evolution (left inset) and devolution (right inset) are illustrated.
Panel A in Figure 6.6 shows the spooling ECL spectra as a function of the applied potential. This technique that we have coined as spooling ECL spectroscopy, allows one to track the changes in the ECL emission peak wavelength and intensity with the corresponding potential. The spooling spectra were obtained within 66 seconds, with an interval of 1 s in the course of 2 cycles of potential scanned from -0.327 V to 1.325 V and back to -0.327 V, at a scan rate of 100 mVs\(^{-1}\). The corresponding cyclic voltammogram, which is dominated by the oxidation of relatively high concentration of TPrA, is shown in panel B. The color-coding represents correlations of the spooling ECL spectra to the potential on the CV. Additional details about ECL spectral peak positions can be clearly seen when the spectra are plotted as stacked spectra (insets) showing ECL intensity evolution (left inset) and devolution (right inset) with the potential change.

The onset emission was observed at a potential of 0.976 V, with a peak wavelength of 950 nm that was maintained at 1.076 V. As shown in Figure 6.7 A, the ECL spectrum can be fitted to only one single peak. The ECL spectrum was compared with the PL spectrum of Au\(_{25}\) shown in Figure 6.8. The ECL peak wavelength recorded at this potential matches with that (945 nm) of the Au\(_{25}\) PL (Figure 6.7A, black curve). The slight red-shift of the ECL spectrum relative to that of PL is related to self-absorption and inner-filter effect due to the higher concentration of ECL relative to PL studies.\(^1\),\(^2\)
Figure 6.7 Curve-fitted ECL spectra acquired at (A) 1.76 V, (B) 1.276 V, (C) 1.174 V.

Also, shown in Figure 6.8 are the PL spectra of in-situ electrogenerated Au$_{25}^0$ and Au$_{25}^+$ clusters. These spectra were obtained using an in-situ
spectroelectrochemical set up (see Experimental), where a 0.1 mM solution of Au$_{25}^-$ (used to obtain the PL in Figure 6.8A, black) was subjected to preparative electrolysis by applying either a potential of 0.04 V vs. SCE to obtain Au$_{25}^0$ species (Figure 6.8A, green curve) or a more positive potential (0.29 V vs. SCE) to further oxidize Au$_{25}^0$ to Au$_{25}^+$ (Figure 6.8A, red curve).

**Figure 6.8 (A)** Photoluminescence spectra of Au$_{25}^-$ (black curve), Au$_{25}^0$ (green curve) and Au$_{25}^+$ (red curve) in 1:1 acetonitrile: benzene mixture with a concentration of 0.67
mg/mL, which were recorded upon excitation with a 532 nm laser. (B) The matching ECL spectra of Au$_{25}^-$/TPrA [12.5 mM] at three applied potentials.

At the onset potential of 0.976 V, Au$_{25}^{2+}$ was generated from Au$_{25}^-$ via sequential oxidation reactions in the vicinity of the electrode (Figure 6.4). At the same potential the local concentration of TPrA$^*$ concentration (orange solid circle on the cyclic voltammogram in Figure 6.6B) was much higher than that of Au$_{25}^{2+}$ (recall that TPrA bulk concentration was 125 times higher than Au$_{25}^-$). The TPaA radical cation generated in eq. 6.1 might have involved the reduction reactions as well. Thus, the electrogenerated Au$_{25}^{2+}$ was reduced by the TPrA radical (by filling an electron in one of its empty HOMO orbitals), eventually producing Au$_{25}^{2-}$ (eq. 6.3). The electro- and chemically generated Au$_{25}^{2+}$ and Au$_{25}^{2-}$ can react, generating Au$_{25}^{*-}$ (eq. 6.4) that returned to the ground state and emitted light at 950 nm (eq. 6.5). While TPrA$^*$ could react with Au$_{25}^{2+}$ to generate Au$_{25}^{+*}$ by injecting an electron in one of its empty LUMOs, the limited concentration of the reacting species Au$_{25}^{2+}$ near the electrode seemed to undergo several successive reduction reactions with TPrA$^*$ to Au$_{25}^{2-}$, since no other excited species were observed at the onset potential and the corresponding peak can be just fitted with one peak (vide infra). Upon applying a more positive potential, the ECL peak was blue-shifted and its intensity increased. For instance, at 1.276 V, the correlated ECL spectrum showed a peak wavelength of 900 nm, while there was a moderate increase in the ECL intensity (green spectrum in Figure 6.8B). At this potential the Au$_{25}^-$ was oxidized to Au$_{25}^{2+}$ (eqs. 6.6-8), which was then reduced to Au$_{25}^+$ (via Au$_{25}^{+*}$) by the TPrA radical. At these higher concentrations of the TPrA radical the Au$_{25}^+$ is reduced further to Au$_{25}^{0*}$; eqn (6.9) and (6.10). The emission of this excited species is at 900 nm, which is in agreement with the PL peak wavelength (Figure 6.6, Figure 6.7B and Figure 6.8A) (eq. 6.11) of the in-situ formed Au$_{25}^{0}$. At this potential the TPrA concentration depletion caused a decrease in the excited state concentration and corresponding emission. The alternative route for Au$_{25}^{0*}$ formation could be electron exchange between Au$_{25}^{2+}$ and Au$_{25}^{2-}$ (eq. 6.4), which
should play a minor role in the emission because of the short lifetime of these two species. The complexity of the proposed mechanisms can be also explored following the simulation techniques.\(^\text{29}\)

\[
T \text{Pr}A \rightarrow T \text{Pr}A^+ + e \quad (4.1)
\]

\[
T \text{Pr}A^+ \rightarrow T \text{Pr}A^* + H^+ \quad (4.2)
\]

\[
\text{Au}^{2+}_{25} + T \text{Pr}A^* \rightarrow \text{Au}^{2+}_{25} + \text{Pr}_2 N^+ = CHCH_2CH_3 \quad (4.3)
\]

\[
\text{Au}^{2+}_{25} + \text{Au}^{2+}_{25} \rightarrow \text{Au}^{*+}_{25} + \text{Au}^{*+}_{25} \quad (4.4)
\]

\[
\text{Au}^{2+}_{25} \rightarrow \text{Au}^{0+}_{25} + h\nu_1 \quad (4.5)
\]

\[
\text{Au}^{0+}_{25} \rightarrow \text{Au}^{0+}_{25} + e \quad (4.6)
\]

\[
\text{Au}^{0+}_{25} \rightarrow \text{Au}^{0+}_{25} + e \quad (4.7)
\]

\[
\text{Au}^{2+}_{25} \rightarrow \text{Au}^{2+}_{25} + e \quad (4.8)
\]

\[
\text{Au}^{2+}_{25} + T \text{Pr}A^* \rightarrow \text{Au}^{*+}_{25} + \text{Pr}_2 N^+ = CHCH_2CH_3 \quad (4.9)
\]

\[
\text{Au}^{0+}_{25} + T \text{Pr}A^* \rightarrow \text{Au}^{0+}_{25} + \text{Pr}_2 N^+ = CHCH_2CH_3 \quad (4.10)
\]

\[
\text{Au}^{0+}_{25} \rightarrow \text{Au}^{0+}_{25} + h\nu \quad (4.11)
\]

Upon reversing the potential scanning direction to cathodic, spooling ECL spectra revealed a significant emission enhancement with no appreciable change in the ECL peak wavelength relative to that of \(\text{Au}^{0+}_{25}\) emission. In this potential range, there would be just enough electrogenerated TPrA\(^+\) to react with \(\text{Au}^{2+}_{25}\). The ET between these two species, resulted in electron injection to the LUMO orbital of the \(\text{Au}^{2+}_{25}\) forming the \(\text{Au}^{*+}_{25}\) excited state (eq. (6.12)) and \(\text{Au}^{+}_{25}\) as in eq. 6.9. The \(\text{Au}^{*+}_{25}\) emitted with a high intensity as shown in the PL experiment (red in Figure 6.8A) at a similar wavelength to that of \(\text{Au}^{0+}_{25}\) (900 nm) (eq. 6.13).

\[
\text{Au}^{2+}_{25} + T \text{Pr}A^* \rightarrow \text{Au}^{*+}_{25} + \text{Pr}_2 N^+ = CHCH_2CH_3 \quad (4.12)
\]

\[
\text{Au}^{*+}_{25} \rightarrow \text{Au}^{+}_{25} + h\nu \quad (4.13)
\]

\[
\text{Au}^{+}_{25} + T \text{Pr}A^* \rightarrow \text{Au}^{0+}_{25} + \text{Pr}_2 N^+ = CHCH_2CH_3 \quad (4.14)
\]

\[
\text{Au}^{0+}_{25} + T \text{Pr}A^* \rightarrow \text{Au}^{0+}_{25} + \text{Pr}_2 N^+ = CHCH_2CH_3 \quad (4.15)
\]
To verify the above assessment on the ECL wavelength and intensity pattern, the ECL spectra at 1.076 V, 1.276 V, and 1.174 V (Figure 6.8B) were plotted along with the PL spectra of the three clusters (Figure 6.8A). Photoinduced Au$_{25}^{−*}$ (black curve in Figure 6.8A) emitted at a peak wavelength of 950 nm, which can be distinguished from that of 865 nm (green curve) of the Au$_{25}^{0*}$ and that of 860 nm (purple curve) from the Au$_{25}^{+*}$. The PL from the Au$_{25}^{+*}$ was more intense than that from the Au$_{25}^{0*}$. Interestingly, ECL from the Au$_{25}^{−*}$, Au$_{25}^{0*}$ and Au$_{25}^{+*}$ were elucidated at the above three applied potentials and they showed the same changes in the wavelength and intensity as observed in the PL; this further validates our assignments.

The ECL-voltage curve of the above system is shown in Figure 6.9, where the ECL intensity measured as photocurrent by a photomultiplier tube (PMT) is plotted vs. the applied potential.

![Figure 6.9](image)

**Figure 6.9** ECL-Voltage curve of 0.1 mM Au$_{25}^-$ in the presence of 12.5 mM TPrA in 1:1 acetonitrile: benzene containing 0.1 M TBAP. Scan rate was at 100 mVs$^{-1}$.

The onset ECL was found to be at 0.876 V, a value in very good agreement with that from the spooling ECL spectroscopy demonstrated above. Less information can be obtained from the ECL-voltage curve than the spooling ECL spectroscopy,
because it detects only the total emitted photons. It is noteworthy that in the absence of \( \text{Au}_{25}^- \) no ECL was observed in a 50 mM TPrA solution (Figure 6.10) in the same potential window.

**Figure 6.10** ECL-Voltage curve of 50 mM tri-\( n \)-propylamine (TPrA) in 1:1 acetonitrile:benzene mixture containing 0.1 M tetra-\( n \)-butylammonium perchlorate. Scan rate was at 100 mVs\(^{-1}\).

The spooling ECL spectra of 0.1 mM of \( \text{Au}_{25}^- \) solution in the presence of other TPrA concentrations (6.3, 25, 50 and 100 mM) were also examined in a similar way, which are shown in Figures S6.1-4. Similar results to those with 12.5 mM TPrA were obtained, namely an emission at 950 nm from \( \text{Au}_{25}^-^* \) at the onset and then at 900 nm, albeit the ECL intensity varied with the TPrA concentration, following the same mechanisms as those with 12.5 mM TPrA concentration. With higher concentrations, at higher applied potentials the ECL peak clearly shifted to 900 nm, which was assigned to the \( \text{Au}_{25}^{0*} \) emission based on what we described above (see the stacked ECL spectra in the insets of Figures S6.2). At potentials favouring the presence of \( \text{Au}_{25}^{2+} \) in the vicinity of the working electrode, \( \text{Au}_{25}^{++} \) formed (eq. 6-12) and the ECL intensity was enhanced at 900 nm. This shift occurs
at 1.076 V for a TPrA concentration of 12.5 mM (Figure 6.6), while at 0.976 V for TPrA concentrations of 25 mM (Figure S6.2) and 50 mM (Figure S6.3).

With the augmented TPrA concentration, the TPrA$^+$ concentration also increases and this favours the reduction reaction of Au$_{25}^+$ (eq. 6.9) to generate the Au$_{25}^{0*}$ (eq. 6.10). On the other hand, the ECL intensity enhancement appeared constantly at 1.127 V after switching the potential scanning direction, indicating that the formation of Au$_{25}^{+*}$ (eq. 6.12) was dominant after consuming some TPrA$^+$ concentration. Figure S6.4 shows the spooling ECL spectra of Au$_{25}^-$ in the presence of 100 mM TPrA. The left inset of the spectra indicates gradual shift of the ECL peak wavelength to 900 nm during the light evolution, while the right inset of the spectra illustrates sequential peak wavelength shift back to 950 nm.

Due to the high reduction power of the electrogenerated TPrA$^+$ species, it can easily act as reducing agent in the bulk solution at higher concentration, and convert the Au$_{25}^-$ to Au$_{25}^{2-}$. With further increased TPrA concentration, to 200 mM for instance, spooling ECL spectra of 0.1 mM Au$_{25}^-$ showed a unique peak wavelength at 983 nm, Figure 6.11. The very high [TPrA$^+$] profile with high reducing power kept the Au$_{25}$ oxidation state as the Au$_{25}^{2-}$ (eqs. 6.9, 6.14, 6.15 and 6.3) in the diffusion layer near the bulk (eq. 6.3). Au$_{25}^{2+}$ immediately generated in the vicinity of the electrode met and reacted with the Au$_{25}^{2-}$, favouring the Au$_{25}^{-*}$ generation, eq. 6.4. This leads to evolution and devolution of ECL at the same wavelength.
Figure 6.11 Spooling ECL spectra of 0.1 mM Au$_{25}^-$ in the presence of 200 mM TPrA. Other measuring conditions are the same as in Figure 6.6. Insets represent stack spectra of ECL evolution (on the left) and devolution (on the right) for clarity of the corresponding peak wavelengths.

The depicted ECL spectrum pattern can be considered as the emission transitions among the three excitation states: ECL is attributed to the Au$_{25}^{-*}$, Au$_{25}^{0*}$ and Au$_{25}^{+*}$ at low TPrA concentrations and that from the Au$_{25}^{-*}$ is dominant at very high TPrA concentration.

Figure 6-12 illustrates accumulated ECL spectra recorded during the potential scanning from -0.33 to 1.33 V vs. SCE in two consecutive cycles.
Figure 6.12 Typical accumulated ECL spectra in the course of potential scanning between -0.324 and 1.324 V vs. SCE in the presence of various TPrA concentrations (A-F) with 6.3, 12.5, 25, 50, 100, and 200 mM, respectively. The spectra were obtained within 2 cycles of scanning or 66 s at a scan rate of 100 mVs⁻¹.

There is an interesting trend with the addition of increased TPrA concentration. Basically, there is no pronounced change in peak wavelength with [TPrA] in the concentration range of 6.3 and 50 mM (Figure 6.12A-D), with a nominal peak wavelength of 910 nm. The apparent peak wavelength in the presence of 100 mM TPrA (Figure 6.12E) was shifted to 950 nm, while it was 983 nm with 200 mM [TPrA] (Figure 6.12F). The trend of the ECL peak shifting is in agreement with the
observed features through the spooling experiments described above, moving to a longer wavelength with the increased TPrA concentration from 6.3 to 200 mM. However, spooling ECL spectroscopy provides much more detailed information on ECL mechanisms.

The ECL efficiency was determined as the photons emitted per redox event relative to the Ru(bpy)$_3^{2+}$/TPrA system (Table 6-1).

**Table 6-1** ECL efficiencies of the Au$_{25}^-$/TPrA system with various TPrA concentrations relative to those of the Ru(bpy)$_3^{2+}$/TPrA with the corresponding TPrA concentrations.$^{13}$

<table>
<thead>
<tr>
<th>[TPrA]/ mM</th>
<th>eff. by PMT %</th>
<th>eff. by camera %</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3</td>
<td>0.0013</td>
<td>2.9</td>
</tr>
<tr>
<td>12.5</td>
<td>0.0005</td>
<td>4.0</td>
</tr>
<tr>
<td>25</td>
<td>0.0045</td>
<td>7.4</td>
</tr>
<tr>
<td>50</td>
<td>0.0156</td>
<td>68.3</td>
</tr>
<tr>
<td>100</td>
<td>0.0203</td>
<td>111</td>
</tr>
<tr>
<td>200</td>
<td>1.9</td>
<td>114</td>
</tr>
</tbody>
</table>

Due to the depleted PMT sensitivity in the NIR region, the strong ECL might be underestimated. It is plausible that the ECL quantum yields measured by the Andor camera and Acton spectrograph set are more reliable. The Au$_{25}^-$/TPrA ECL efficiencies determined using the latter CCD camera for different [TPrA] are provided in Table 6-1; for example the relative ECL efficiency at [TPrA] = 50 mM is 68.3%. Please also note that with high [TPrA], the ECL quenching in the Ru(bpy)$_3^{2+}$/TPrA coreactant system was more dramatic than that in the Au$_{25}^-$/TPrA one.$^3$ That is the reason why the relative efficiency in Table 6-1 probably shows overestimated efficiencies with [TPrA] larger than 100 mM. Needless to say, the


Au\textsubscript{25}\textsuperscript{−}/TPrA coreactant system should have an ECL efficiency > 50% relative to the Ru(bpy)\textsubscript{3}\textsuperscript{2+}/TPrA.

While the above Au\textsubscript{25}\textsuperscript{−}/TPrA coreactant system did produce intermediate ECL intensity, the generation mechanisms showed a zigzagged energy pathway: oxidation of TPrA (eq. 6-1) and sequential oxidation Au\textsubscript{25}\textsuperscript{−} to Au\textsubscript{25}\textsuperscript{2+} (eqs. 6.6-8) for generating active radicals, and then successive reduction of Au\textsubscript{25}\textsuperscript{2+} to Au\textsubscript{25}\textsuperscript{+} by TPrA\textsuperscript{*} (eq. 6.9) in the vicinity of the electrode and reduction of Au\textsubscript{25}\textsuperscript{−} to Au\textsubscript{25}\textsuperscript{2−} (eq. 6.3) in the bulk for the final generation of the possible three excited states Au\textsubscript{25}\textsuperscript{−}\textsuperscript{*} (eq. 6.4), Au\textsubscript{25}\textsuperscript{0\textsuperscript{*}} (eqs. 6.10) and Au\textsubscript{25}\textsuperscript{+\textsuperscript{*}} (eq. 6.12). While the ECL onset potentials favours the Au\textsubscript{25}\textsuperscript{−}\textsuperscript{*} generation, the processes to electrogenerate the other two excited states are rather complex, involving many body reactions. Because of the presence of a reduction peak at \textasciitilde 1.5 V for Au\textsubscript{25}\textsuperscript{−}/Au\textsubscript{25}\textsuperscript{2−}, it is natural to take considerations of scanning the applied potential in the cathodic region with an electrogenerated oxidative co-reactant such as benzoyl radical (BPO\textsuperscript{*} with E\textsuperscript{°} > +1.5 V vs. SCE\textsuperscript{14}). The electrogenerated BPO radical can react with Au\textsubscript{25}\textsuperscript{2−} to form the Au\textsubscript{25}\textsuperscript{−}\textsuperscript{*} excited state. In this manner, the zigzagged energy pumping can be avoided.

6.3.3 Electrochemiluminescence of Au\textsubscript{25}\textsuperscript{−} in the presence of benzoyl peroxide

In the Au\textsubscript{25}\textsuperscript{−}/BPO co-reactant system, the reduction of Au\textsubscript{25}\textsuperscript{−} to Au\textsubscript{25}\textsuperscript{2−} and the reduction of BPO to produce the oxidizing benzoate radical occurred at very similar potentials, hopefully leading to a more efficient generation of Au\textsubscript{25}\textsuperscript{−}\textsuperscript{*} than that from the Au\textsubscript{25}\textsuperscript{+}/BPO co-reactant system we previously published\textsuperscript{13}. The electrogeneration of Au\textsubscript{25}\textsuperscript{2−} from the bulk Au\textsubscript{25}\textsuperscript{−} can happen in smaller potential window rather than reduction of Au\textsubscript{25}\textsuperscript{+}. Figure 6.13 shows the ECL-voltage curve (A) and corresponding cyclic voltammogram (CV) (B) of 0.1 mM Au\textsubscript{25}\textsuperscript{−} with 5 mM BPO. The applied potential was scanned from -0.167 V vs. SCE towards more negative values.
Figure 6.13 (A) ECL-voltage curve and (B) cyclic voltammogram of 0.1 mM Au$_{25}^-$ in the presence of 5 mM benzoyl peroxide (BPO) at a scan rate of 100 mVs$^{-1}$. The cross indicates starting potential.

The onset of ECL-Voltage curve was found to be -0.655 V, at which the BPO reduction (eq. 6.16) began. The reduction reaction was followed by a decomposition reaction (eq. 6.17) to the benzoate radical (C$_6$H$_5$CO$_2^•$). The peak at -0.8 V is similar to the previously observed for the Au$_{25}^+/\text{BPO}$ co-reactant system, while here it is more pronounced due to the different co-reactant concentration, can be generated prior to the reduction of the luminophore.$^{13}$ Similar to the Au$_{25}^+/\text{BPO}$ co-reactant system,$^{13}$ C$_6$H$_5$CO$_2^•$ accepted one electron from the Au$_{25}^-$ and transformed it to Au$_{25}^0$ (eq. 6.18). The Au$_{25}^-^*$ excited state could be generated by transferring one electron from an available reducing
species to the LUMO of $\text{Au}_{25}^0$ (eq. 6.18), releasing light upon relaxation to the ground state (eq. 6.20).

$$BPO + e \rightarrow BPO^- \quad (4.16)$$

$$BPO^- \rightarrow C_6H_5CO_2^+ + C_6H_5CO_2^- \quad (4.17)$$

$$C_6H_5CO_2^+ + \text{Au}_{25}^- \rightarrow \text{Au}_{25}^0 + C_6H_5CO_2^- \quad (4.18)$$

$$\text{Au}_{25}^0 + BPO^- \rightarrow \text{Au}_{25}^* + BPO \quad (4.19)$$

$$\text{Au}_{25}^- + e \rightarrow \text{Au}_{25}^{2-} \quad (4.20)$$

$$C_6H_5CO_2^+ + \text{Au}_{25}^{2-} \rightarrow \text{Au}_{25}^* + C_6H_5CO_2^- \quad (4.21)$$

Further sweeping the potential to negative values, ECL intensity continued to increase because the reactions showed by eqs. 6.18 and 6.19 were favoured. The ECL intensity reached a maximum at -1.300 V at which potential the benzoate radical formation is at the highest. Continuously moving the potential more negative lead to the reduction of $\text{Au}_{25}^-$ to $\text{Au}_{25}^{2-}$ (eq. 6.20 and Figure 6.4). The $\text{Au}_{25}^*$ was generated in this potential region by the reaction of $\text{Au}_{25}^{2-}$ with $C_6H_5CO_2^-$ in the diffusion layer (eq. 6.21). The ECL intensity reached the highest at the applied potential of -1.582 V as the result of the balance between the rise of $[\text{Au}_{25}^{2-}]$ and depletion of BPO.

NIR ECL light emission in this system occurred at 950 nm upon relaxation of the $\text{Au}_{25}^*$ to the ground state (eq. 6.5), which was confirmed by spooling ECL spectroscopy illustrated in Figure 6.14.
Figure 6.14 Spooling spectra of 0.1 mM Au$_{25}^-$ in the presence of 5 mM benzoyl peroxide (BPO). The applied Potential was scanned at 100 mVs$^{-1}$ from -0.167 to 1.85 and back to 0.353 V within 83 seconds. Insets are evolution (the red) and devolution (the blue) spectra of the first cycle.

It is important to note that the Au$_{25}^-$/BPO co-reactant system would be more favourable than the corresponding Au$_{25}^+$/BPO, and higher ECL intensity is anticipated. Figure 6.14 shows the recorded spooling ECL spectra of the Au$_{25}^-$/BPO co-reactant system during two consecutive potential scanning cycles from -0.358 to -2.1 and to 1.62 V. Importantly, the onset ECL spectrum was recorded at -0.655 V, in very good agreement with that of ECL-voltage in Figure 6.13. As shown in stacked spectra for ECL revolution and devolution, the ECL peak wavelength is constant at 950 nm. This means that the emission is originated from the same Au$_{25}^-$* excited state. The ECL emission of Au$_{25}^-$/TPrA system reached to 170 count, which is three times higher than the Au$_{25}^-$/BPO system with the same coreactant concentration. The BPO concentration was varied from 2.5 to 25 and 50 mM (Figures S6.5-7). The lower 2.5 mM concentration did not generate enough of the required BPO radical to observe ECL. In the presence of 25 and 50 mM the intensity of the ECL light emission is low due to the quenching effect of the
coreactant. Thus, the best ECL efficiency with 5 mM BPO was estimated > 30% relative to the Ru(bpy)$_3$$^{2+}$ system (Table 6-2).

**Table 6-2** ECL efficiencies of the Au$_{25}^-$/BPO system with various BPO concentrations relative to those of the Ru(bpy)$_3$$^{2+}$/BPO with the corresponding BPO concentrations.

<table>
<thead>
<tr>
<th>[BPO]/ mM</th>
<th>eff. by PMT%</th>
<th>Eff. by Camera%</th>
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</tr>
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### 6.4 Conclusion

For the first time, ECL of the Au$_{25}^-$ cluster was studied in both annihilation and co-reactant routes. No appreciable ECL was observed in the annihilation path, due to the low reaction rate of the two cluster cores and the short lifetime of the electrogenerated reactive intermediates, the Au$_{25}^{2-}$ and Au$_{25}^{2+}$. In the presence of TPrA or BPO as the co-reactant, a relatively long-lived strong reducing or oxidizing intermediate was electrogenerated, which can react with various Au$_{25}$ charged species to give off NIR-ECL. The Au$_{25}^-$/TPrA system showed ECL emissions at 950 and 900 nm. By means of spooling ECL spectroscopy, the two-wavelength ECL was attributed to three excitation states including Au$_{25}^{-*}$, Au$_{25}^{0*}$ and Au$_{25}^{+*}$. These were elucidated by comparing the ECL spectra with PL spectra measured with each of the species generated *in-situ*. Interestingly, the ECL intensity is proportional to the local concentration of these excited states and can be tuned by the applied potential or co-reactant concentration. BPO also enhanced the ECL emission at 950 nm in the NIR region. The study of ECL dependence on the TPrA and BPO concentration revealed that the TPrA system is more efficient than BPO. In the current study, the Au$_{25}^-$/ BPO system is more efficient than our previous Au$_{25}^+$/ BPO
system, due to the smaller driving force needed for $\text{Au}_{25}^{2-}$ generation. These fundamental studies add to the knowledge of the properties of these interesting small old nanoclusters and the ECL of these nanoclusters is anticipated to have potential applications in electroanalytical sensing and bio-imaging.\textsuperscript{31}

6.5 References


Chapter 7

Summary and Future Work

As highlighted in this thesis, ECL is an applicable technique in the field of analytical chemistry with great sensitivity and tenability. Au nanoclusters possess interesting “molecular-like” properties such as their optical, electrochemical, and catalytic properties, especially their unique NIR light emissions. The research presented here has demonstrated highly efficient NIR ECL from Au$_{144}$(SC$_2$H$_4$Ph)$_{60}$, Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ and Au$_{25}$(SC$_2$H$_4$Ph)$_{18}$$^z$ ($z$ =1-, 0 and 1+) nanoclusters. Also, the thermodynamic and kinetic origins of Au$_{25}$(SC$_2$H$_4$Ph)$_{18}$$^z$ by means of spooling ECL and PL spectroscopy newly developed in this thesis.

The Au$_{144}$(SC$_2$H$_4$Ph)$_{60}$/TPrA coreactant system showed an enhanced NIR ECL relative to the nanocluster annihilation process. The ECL mechanisms were explored using conventional ECL-voltage curves along with our newly introduced spooling ECL spectroscopy. It is interesting to note that the NIR ECL emissions are tunable with the applied potential.

The calculated electronic structure of the Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ nanocluster was found to be well-matched with its electrochemical and optical features. While highly efficient NIR ECL was obtained for the Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$/TPrA coreactant system, mild ECL was observed in Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$/BPO coreactant system due to the rich electrochemistry of this nanocluster.

All three charged states of Au$_{25}$(SC$_2$H$_4$Ph)$_{18}$ nanoclusters were discovered to release strong NIR-ECL. A large investigation was undertaken correlating kinetic parameters such as the coreactant concentrations and applied potentials to the ECL
wavelength and intensity from negatively and positively charged \( \text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18} \) nanoclusters. The thermodynamic origin of the nanocluster ECL was explored by means of the Latimer diagram.

For the neutral \( \text{Au}_{144}(\text{SR})_{60} \), \( \text{Au}_{38}(\text{SR})_{24} \) and \( \text{Au}_{25}(\text{SR})_{18} \) nanoclusters, the obtained ECL intensity followed the order as \( \text{Au}_{38}(\text{SR})_{24} > \text{Au}_{25}(\text{SR})_{18} > \text{Au}_{144}(\text{SR})_{60} \). This tendency can be correlated to their structures and their reactive sites. This is plausible that the uncovered position of the gold core of the nanoclusters are more chemically reactive. Within the \( \text{Au}_{25} \) nanoclusters family (with similar size and structure, but different charge states) the ECL intensity followed the order as \( \text{Au}_{25}^+ > \text{Au}_{25}^0 > \text{Au}_{25}^- \). One can correlate the ECL intensity pattern in this series to the probability for the promoted electron to relax back from their LUMO to HOMO.

Additionally, PL spectra of various charge states of \( \text{Au}_{144}(\text{SC}_2\text{H}_4\text{Ph})_{60} \), \( \text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24} \) and \( \text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18} \) nanoclusters were reported for the first time using spooling PL spectroscopy. Changes in the PL peak wavelengths, and intensity were determined for the different charge states, which helped identifying the ECL emitting species and mapping out the ECL mechanisms.

The resulting NIR ECL emission has potential application for tissue and cell imaging, where it will not be absorbed. Furthermore, Quantum dots (QDs), which have been used extensively in the NIR PL immunoassay sensors, could be replaced by the Au nanoclusters. The strong ECL emissions of the Au clusters can be used for ion selective detection. For example there are several ions such as \( \text{Cu}^{2+} \), \( \text{Ag}^+ \), \( \text{Pt}^{2+} \), \( \text{Pd}^{2+} \), and \( \text{Hg}^{2+} \) that have shown reactions with gold clusters. They can be the target ions to react with the Au clusters, leading to enhancement or quenching of the resulting ECL emissions. The work in this thesis might set some guidelines for new investigations and applications of the Au nanocluster NIR-ECL. Also, based on the obtained results, a series of ECL simulations can be performed in the future to gain more insight into the kinetic origin of the observed ECL processes.
Appendices

Appendix A: Chapter 2: Electrogenated chemiluminescence of monodispersed Au_{144}(SC_{2}H_{4}Ph)_{60} clusters.

![ECL-voltage curve](image)

**Figure S2.0.1** ECL-voltage curve of 50 mM TPrA in 1:1 benzene: acetonitrile containing 0.1 M TBAP (and without added Au_{144} as a control) during annihilation at a scan rate of 50 mVs^{-1}.
Appendix B: Chapter 3: Highly Efficient Electrogenerated chemiluminescence of Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ clusters
Figure S3.1 Top: ECL-Voltage curve of 0.1 mM Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ in 1:1 acetonitrile :benzene mixture containing 0.1 M TBAP in the presence of 12.5 mM tri-$n$-propylamine (TPrA). Bottom: spooling ECL spectra of 0.1 mM Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ in the same electrolyte solution with scan rate of 100 mV/s. The potential window was between -0.51 and 1.3 V vs. SCE and each spectrum was acquired in 1 s time interval. The insets show stacked spectra for ECL evolution and devolution during the scanning of the applied potential.
Figure S3.2 Top: ECL-Voltage curve of 0.1 mM Au_{38}(SC_{2}H_{4}Ph)_{24} in 1:1 acetonitrile :benzene mixture containing 0.1 M TBAP in the presence of 25 mM tri-n-propylamine (TPrA). Bottom: spooling ECL spectra of 0.1 mM Au_{38}(SC_{2}H_{4}Ph)_{24} in the same electrolyte solution with scan rate of 100 mV/s. The potential window was between -0.51 and 1.3 V vs. SCE and each spectrum was acquired in 1 s time interval. The insets show stacked spectra for ECL evolution and devolution during the scanning of the applied potential.
Figure S3.3 Top: ECL-Voltage curve of 0.1 mM Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ in 1:1 acetonitrile :benzene mixture containing 0.1 M TBAP in the presence of 100 mM tri-$n$-propylamine (TPrA). Bottom: spooling ECL spectra of 0.1 mM Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ in the same electrolyte solution with scan rate of 100 mV/s. The potential window was between -0.51 and 1.3 V vs. SCE and each spectrum was acquired in 1 s time interval. The insets show stacked spectra for ECL evolution and devolution during the scanning of the applied potential.
Figure S3.4 Top: ECL-Voltage curve of 0.1 mM $\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}$ in 1:1 acetonitrile :benzene mixture containing 0.1 M TBAP in the presence of 200 mM tri-$n$-propylamine (TPrA). Bottom: spooling ECL spectra of 0.1 mM $\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}$ in the same electrolyte solution with scan rate of 100 mV/s. The potential window was between -0.51 and 1.3 V vs. SCE and each spectrum was acquired in 1 s time interval. The insets show stacked spectra for ECL evolution and devolution during the scanning of the applied potential.
As an example, ECL efficiency values were calculated by integrating ECL spectrum vs. wavelength and the corresponding cyclic voltammogram vs. time, and comparing the integrated ECL intensities (equivalent to the number photons) and the current values (charges) of the \( \text{Au}_{38} \)/TPrA samples with those of the reference \( \text{Ru(bpy)}_3^{2+} \)/TPrA during the ECL experiments. The quantum yield was calculated using the equation below:

\[
\Phi_x = 100 \times \left( \frac{\int_a^b \text{ECL} \, dt}{\int_a^b \text{Current} \, dt} \right)_x \left/ \left( \frac{\int_a^b \text{ECL} \, dt}{\int_a^b \text{Current} \, dt} \right)_S \right.
\]

where \( \Phi \) is the quantum yield (\%) relative to the \( \text{Ru(bpy)}^{2+} \)/TPrA, ECL is the ECL intensity, current is the electrochemical current value, \( S \) is the standard (the \( \text{Ru(bpy)}^{2+} \)/TPrA) and \( x \) is the sample (the \( \text{Au}_{38} \)/TPrA). Table 3-1 shows calculated values for each TPrA concentration.\(^1\)

The R980 PMT detector does not respond well after 830 nm (less than 0.1% in QE, Figure S3.5) for the Au clusters, while it has a high QE of 7.5% for \( \text{Ru(bpy)}_3^{2+} \) emission at 650 nm. The ECL efficiency for the \( \text{Au}_{38} \)/TPrA co-reactant system relative to that for the \( \text{Ru(bpy)}_3^{2+} \)/TPrA is then underestimated.

It is fortunate to see that the Andor iDUS BR-DD CCD camera has very similar response for both the \( \text{Ru(bpy)}_3^{2+} \) (emission at 650 nm) and \( \text{Au}_{38}^- \) (emission at 930 nm) (red in Figure S3.6). The ECL quantum yields measured by this camera and Acton spectrograph set are more reliable.
Figure S3.5 The spectral response curve, 562U for Hamamatsu R928 PMT used in our PL spectrometer.

Figure S3.6 The iDus CCD camera response curve (BR-DD, red).
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Author: Mahdi Hesari, Mark S. Workentin, Zhifeng Ding

Publication: ACS Nano

Publisher: American Chemical Society

Date: Aug. 1, 2014

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Appendix C: Chapter 4: Near-infrared electrochemiluminescence from \( \text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}^+ \) clusters co-reacted with tri-\( n \)-propylamine.

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Appendix D: Chapter 5: Thermodynamic and Kinetic Origins of Au$_{25}^0$ Nanocluster Electrochemiluminescence

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Figure S5.1 Stacked spooling PL spectra at a time interval of 20 s in the course of electrolysis of a 0.1 mM $\text{Au}_{25}^0$ solution to the destiny oxidation states, $\text{Au}_{25}^+$, $\text{Au}_{25}^{2+}$, $\text{Au}_{25}^-$ (A-C) and $\text{Au}_{25}^{-2}$ shows spooling PL spectra at a time interval of 20 s in the course of electrolysis of a 0.1 mM $\text{Au}_{25}^0$ solution to the destiny oxidation states $\text{Au}_{25}^{-2}$. 
Figure S5.2 ECL-voltage curves measured on the R928 PMT and corresponding cyclic voltammograms of Au$_{25}^0$ in the presence of (A) 6.3, (B) 25, (C) 50, (D) 100, (E) 200 mM TPrA, recorded by 4 cycles between -0.30 and 1.23 V vs. SCE at scan rate of 100 mVs$^{-1}$. 
Appendix E: Chapter 6: NIR Electrochemiluminescence from Au$_{25}^-$ Clusters Facilitated by Highly Oxidizing and Reducing Coreactant Radicals.

**Figure S6.1** Spooling ECL spectra and stacked spectra for 0.1 mM Au$_{25}^-$ in the presence of 6.3 mM TPrA, recorded in 1:1 acetonitrile: benzene, containing 0.1 M TBAP. The scan rate was at 0.1 V s$^{-1}$, and an Andor BR-DD CCD camera (cooled at -65 °C) was used.

**Figure S6.2** Spooling ECL spectra and stacked spectra for 0.1 mM Au$_{25}^-$ in the presence of 25 mM TPrA, recorded in 1:1 acetonitrile: benzene, containing 0.1 M TBAP. The scan rate was at 0.1 V s$^{-1}$, and an Andor BR-DD CCD camera (cooled at -65 °C) was used.
Figure S6.3 Spooling ECL spectra and stacked spectra for 0.1 mM Au$_{25}^-$ in the presence of 50 mM TPrA, recorded in 1:1 acetonitrile: benzene, containing 0.1 M TBAP. The scan rate was at 0.1 V/s, and an Andor BR-DD CCD camera (cooled at -65 °C) was used.

Figure S6.4 Spooling ECL spectra and stacked spectra for 0.1 mM Au$_{25}^-$ in the presence of 100 mM TPrA, recorded in 1:1 acetonitrile: benzene, containing 0.1 M TBAP. The scan rate was at 0.1 V/s, and an Andor BR-DD CCD camera (cooled at -65 °C) was used.
Figure S6.5 (A) ECL-voltage curve for 0.1 mM Au$_{25}^-$ in the presence of 2.5 mM benzoyl peroxide (BPO), recorded in 1:1 acetonitrile: benzene, containing 0.1 M TBAP. The scan rate was at 0.1 Vs$^{-1}$. (B) Spooling ECL spectra of the same solution mixture during 62 s as the potential scanning. The inset shows accumulated spectrum. An Andor BR-DD CCD camera (cooled at -65°C) was used.
Figure S6.6 (A) ECL-voltage curve for 0.1 mM Au$_{25}^-$ in the presence of 25 mM benzoyl peroxide (BPO), recorded in 1:1 acetonitrile: benzene, containing 0.1 M TBAP. The scan rate was at 0.1 Vs$^{-1}$. (B) Spooling ECL spectra of the same solution mixture during 62 s as the potential scanning. The inset shows accumulated spectrum. An Andor BR-DD CCD camera (cooled at -65°C) was used.
Figure S6.7 (A) ECL-voltage curve for 0.1 mM Au$_{25}^-$ in the presence of 50 mM benzoyl peroxide (BPO), recorded in 1:1 acetonitrile: benzene, containing 0.1 M TBAP. The scan rate was at 0.1 Vs$^{-1}$. (B) Spooling ECL spectra of the same solution mixture during 62 s as the potential scanning. The inset shows accumulated spectrum. An Andor BR-DD CCD camera (cooled at -65°C) was used.
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