Deciphering the Dual Emission in the Photoluminescence of $Au_{14}Cd(SR)_{12}$: A Theoretical Study using TDDFT and TDDFT+TB

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Abstract:

Determining excited state processes for small nanoclusters (NCs), specifically gold, aids in our ability to fine-tune luminescent materials and optical devices. Using TDDFT and TDDFT+TB, we present a detailed theoretical explanation for the dual emission peaks displayed in $Au_{14}Cd(S\text{-}Adm)_{12}$ (Adm = Adamantane). As dual emission is relatively rare, we decipher whether the mechanism originates from two different excited states, or from two different minima on the same excited state surface. This unique mechanism, which proposes that the dual emission results from two minima on the first excited state, stems from geometrical changes in the bi-tetrahedron core during the emission process.

Introduction:

Understanding photoactive biomolecules, large nanoparticles (NPs) and photoluminescent (PL) species has important applications ranging from solar energy conversion to biosensing.[1-5] In particular, heavy atom transition metals, such as gold, have garnered attention in the physical chemistry community due to the nanoclusters' (NCs) ability to be efficient, selective and easily tuned.[6-9] These NCs also show enhanced PL properties[10-11] which give unique mechanisms and thereby a deeper understanding into functional materials. Several gold NCs have been synthesized in the past decade providing pathways to tune the emission for extensive physical applications. Specific emission can be tuned by changing the particle size, surface ligands and valence states for NCs.[12] Specific examples of tuning photoluminescent properties with surface ligands can be seen through the work of Hui et al. where they discovered that PL enhancement is governed by the formation of smaller Au species etched by thiol groups in AuCyt (Cyt = Cytidine), which is usually quenched due to the close adsorption of the thiol groups to the surface of the gold NC.[13] Wu et al. further studied the effect of surface ligands in thiolate-protected gold NCs and found out that longer Au^{I}-SR motifs can be used to sustain a strong aggregation induced emission pathway, while shorter Au^{I}-SR motifs lead to a larger Au^{0} core allowing the fluorescence from the core of the NC to dominate the PL mechanism.[14] Many groups have also successfully doped their nanoclusters with Cd as a way to tailor the chemical and physical properties such as photoluminescence and surface flexibility.[15-17] Cd doping has been shown to lead to unique mechanisms; for example, $Au_{24}Cd(SC_2H_4Ph)_{18}$ undergoes a S_{N1}-like ligand exchange mechanism due to its stability.[18] Further, it has been shown that by introducing a Cd−Br bond on the surface of gold NCs, large dipole moments can be achieved.[19]

In 2013, Jiang et al. used DFT to predict the geometry of the smallest stable thiolate-stabilized gold nanocluster, $Au_{15}(SR)_{13}$, for the experimentally observed $Au_{15}(SG)_{13}$ (SG = glutathionate) system.[20] This Au_{15} thiolate-protected NC and its derivatives have since been synthesized and studied rigorously; however, due to the flexibility of the SG ligand, it is difficult to obtain the crystal structure.[21] In 2018, Yang et al. tried to obtain the crystal structure of $Au_{15}(SR)_{13}$ via two routes: (1) direct ligand exchange of $Au_{15}(SG)_{13}$, and (2) Cd doping of $[Au_{15}(SG)_{12}]^-$. Through the latter method, $Au_{14}Cd(S\text{-}Adm)_{12}$ (Adm = Adamantane) was found and classified through single crystal X-ray diffraction.[21] $Au_{14}Cd(S\text{-}Adm)_{12}$ has a Au_5Cd bi-tetrahedron core with one shared Au-Cd 'bridging' bond, two tetrameric Au_4S_5 staple motifs and one AuS_2 motif connected to the core. The framework of the tetrameric motifs (figure 1 (c)) gives the NC a boxed four-quadrant appearance from two tetrahedrons sharing an edge, while the AuS_2 motif (figure 1 (d)) caps the core of the NC. Further experimental investigation from Li et al. showed that this NC exhibits rare dual emission behavior, which they attributed to a predicted 'restrained'-type distortion in the core due to one tetrahedron growing/folding up and the other shrinking/folding down upon relaxation.[22] While the experiments hypothesize a photo-induced structural distortion and electronic redistribution, the exact geometric differences and origin of electronic states are unknown. Herein, we directly suggest a PL mechanism for this $Au_{14}Cd$ thiolate-protected NC by exploring the excited state potential energy surfaces from a theoretical perspective.

Figure 1. Crystal structure of $Au_{14}Cd$ NC. Reprinted with permission from JACS ***2018,*** *140 (35), 10988-10994. Copyright 2018 American Chemical Society. (a) Thiolate-protected framework; (b) Au_5Cd bi-tetrahedron core; (c) Two Au_4S_5 tetrameric motifs* (i) *connected to core; (d) AuS_2 staple motif* (ii) *capping the core. The gold atoms are in blue, sulfur atoms are in red, and the Cd atom is in orange. No carbon or hydrogen atoms are shown.*

Computational Details:

All calculations were done using the Amsterdam Density Functional (ADF) 2018.105 package.[23] The crystal structure from Yang et al.[21] was used as an initial input structure for the geometry optimization of $Au_{14}Cd(S\text{-}Adm)_{12}$. $Au_{14}Cd(SR)_{12}$ NCs with R = H and CH_3 were also created by editing the ligands in the crystal structure using the MacMolPlt visualization tool.[24] All geometry optimizations (ground and excited state) were calculated with the local density approximation (LDA) Xalpha exchange-correlation functional[25] and a double zeta (DZ) basis set.[26] All structures were optimized in the gas phase. Scalar relativistic effects were included by utilizing the zeroth-order regular approximation (ZORA).[27-28] The energy and gradient convergence criteria were tightened to $1x10^{-4}$ and $1x10^{-3}$ Hartree respectively for geometric accuracy in closed shell calculations, and the gradient convergence criteria was loosened to $2x10^{-3}$ Hartree for open shell calculations. After the initial ground state geometry optimization, a linear response time-dependent density-functional theory plus tight binding[29] (TDDFT+TB) calculation was run to obtain vertical excitation energies, which were then convolved into the optical absorption spectrum with a Gaussian fit and a 0.20 eV full width half maximum (FWHM). Similar results were obtained through TDDFT[30] as a comparison for excited state methodology. Further details about TDDFT+TB are provided in the supporting information. After obtaining the ground state structure and absorption spectrum, TDDFT analytical excited state gradients[31] were used to optimize the minimum energy structures of the excited states.

Results and Discussion:

An important component of excited state potential energy surface (PES) exploration is finding a level of theory that accurately represents the system, while trying to save computational cost. In this work, we first considered whether model ligands are reasonable substitutes for the full S-Adm ligand. In some situations, optical spectra have been found to be similar regardless of ligand;[32-34] in other cases, large optical changes between different ligands can be expected as small gold NCs are more sensitive to the length of the S-Au-S staple motifs.[35] Using the crystal structure from Yang et al.,[21] two model ligands were created by replacing adamantane with hydrogen and methyl groups, respectively. As demonstrated in figure 2, the absorption spectrum is highly dependent on the ligand. Thus, the full S-Adm ligand was used for further computational study.

Figure 2. Theoretical absorption spectrum of Au$_{14}$Cd(SR)$_{12}$ NCs where R = H (blue dotted), CH$_3$ (orange dashed) and S-Adm (green solid) with the Xalpha/DZ level of theory.

Au$_{14}$Cd(S-Adm)$_{12}$ is a chiral compound with C$_2$ symmetry; the C$_2$ axis runs through the gold atom in the AuS$_2$ motif that caps the core. The ground and excited state structures of Au$_{14}$Cd(S-Adm)$_{12}$ were studied for the two enantiomers that differ in the positions of the Au and Cd atoms in the Au-Cd ‘bridging’ bond in the bi-tetrahedron core. Both enantiomers are examined because they are present experimentally and the crystal structure reveals that the Au-Cd ‘bridging’ bond possesses 50% partial occupancy of both atoms;[21] as expected, both enantiomers yield the same linear optical absorption and emission properties as shown in the supplementary material (figures S2-S4 and table S1). Figure 3 shows the molecular structure of both Au$_{14}$Cd(S-Adm)$_{12}$ enantiomers and illustrates the atom switch in the core. As seen in Figure 3, the optimized ground state structures of both isomers are similar to the crystal structure with 12 Adm ligands providing structural rigidity around the shell, a Au$_5$Cd bi-tetrahedron core with a one shared ‘bridging’ bond, two tetrameric Au$_4$S$_5$ staple motifs and one AuS$_2$ motif connected to the Au/Cd core. The average bond distances of the optimized ground state structure (S$_0$) at the Xalpha/DZ level of theory can be seen in table 1, where the atom definitions are illustrated in figure 4. It is important to note that LDA functionals are not the greatest for excited state energies.[36-37] However, LDA functionals are good for geometric parameters, such as bond lengths.[38] Au-Au bond lengths, in particular, have been shown to match well with experiment;[39] for example, the average Au-Au distance from central atom to shell is 2.784 Å at the Xalpha/DZ level of theory, which is very close to the experimental value of 2.782 Å in [Au$_{25}$(SH)$_{18}$]$^-$.[40] This average distance obtained from theory is only 0.86% larger than the Au-Au bond distances between the core atoms of Au$_{14}$Cd(S-Adm)$_{12}$, which is 2.760 ± 0.076 Å. As an additional point of comparison, compared to the Au-Au distance of 2.88 Å in bulk gold,[41] the Au-Au core distances in Au$_{14}$Cd(S-Adm)$_{12}$ are 4.2% shorter. The average Au-Cd bond distance between atoms in the core is 2.833 ± 0.063 Å. The Au-Cd distances in this NC are 1.7% shorter than the Au-Cd distance of 2.88 Å calculated by the relationship between dopant-Au bond length and metallic radii.[42] The M-M bonds (M = Au/Cd) provided in the core of the crystal structure are 2.856 Å on average.[21] The combined average between Au-Cd and Au-Au bonds with theory underestimates this length by 2.2% with an average value of 2.793 ± 0.074 Å.

Figure 3. Optimized ground state geometric structures for the $Au_{14}Cd(S\text{-}Adm)_{12}$ enantiomers. The gold, cadmium, sulfur, carbon, and hydrogen atoms are green, orange, red, black, and white respectively. (A) The entire 327-atom nanocluster with the full S-Adm ligand. (B) The Au_4Cd core with one shared 'bridging' bond between the separate tetrahedrons. (C) Tetrameric framework originating from the Au atoms and thiolate-protected shell.

Figure 4. Atom definitions for table 1.

Average Bond Length (Å)	
Bond	**S_0**
Au core - Au core	2.760 ± 0.076
Au shell - Au shell	2.941 ± 0.101
Au core - Cd core	2.833 ± 0.063
Au shell - S terminal	2.469 ± 0.021
Cd core - S terminal	2.530 ± 0.000
Au shell - S staple	2.401 ± 0.035
S staple - S staple	4.739 ± 0.037

Table 1. The average bond lengths of the ground state geometry at the Xalpha/DZ level of theory.

$Au_{14}Cd(S\text{-}Adm)_{12}$ has a HOMO (H)-LUMO (L) gap of 1.48 eV (figure S5). Upon excitation, the absorption spectrum of the NC exhibits a strong S_1 state that is dominated by the H-L transition, and no other singlet-singlet excitations are present near the energy of the main peak. The molecular orbitals show a superatomic P to D transition in the core of the NC (figure 5A) from the 1.59 eV peak with an oscillator strength of 0.0387; there is also a shoulder that occurs at 2.15 eV. The experimentally observed peak is seen at 2.25 eV (550 nm) with a slight shoulder at 2.95 eV (420 nm).[22] The shape resulting from the convolution of the vertical excitation energies from theory is quite comparable to the experimental absorption spectrum despite the ~0.7 eV underestimation. This underestimation in energy is an expected result for LDA exchange correlation functionals.[43]

Figure 5. (A) HOMO and LUMO molecular orbitals from the Xalpha/DZ level of theory. The HOMO forms a superatomic P shape in the core and the LUMO forms a superatomic D_{z2} shape in the core. Additional views of the HOMO and LUMO are provided in Figure S6. (B) Theoretical absorption spectrum obtained from TDDFT+TB using the Xalpha/DZ level of theory (a comparison between TDDFT+TB and TDDFT spectra is shown in Figure S1). (C) Experimental absorption spectrum (data adapted with permission from Nat. Commun. **11** 2897 (2020)*).*

We can further piece together the PL mechanism by looking at the theoretical emission energies. Exploration of the first excited state potential energy surface shows that the dual emission results from two different minima (which we call S_1 and S_1') on the first electronically excited state. The first minimum point, S_1, was obtained by a geometry optimization of the S_1 state starting from the S_0 optimized geometry. This point has an emission energy of 1.09 eV. The second minimum point, S_1', was obtained by starting the geometry optimization of the S_1 state from a converged point on the S_2 PES (resulting from an S_2 optimization) as illustrated in figure 6A. S_1 is 0.29 eV lower in energy than S_1', and both minima originate from transitions from the P → D superatomic orbitals due to the prominent HOMO-LUMO excitation in the core. The initial input geometry was chosen differently to see if the same minimum point on the S_1 surface would be obtained. As the optimization did not result in the same minimum point, we can conclude that the S_1 state has at least two different minimum points. The emission energy at this point (S_1') is 0.86 eV which is 0.23 eV lower than the emission energy from S_1 (figure 6B). This energy gap is essentially the same as the 0.24 eV gap that was observed between the dual emission peaks in the experimental spectrum;[22] hence, we can conclude that the dual emission is a result of these two points on the S_1 surface. The theoretical Stokes shifts are 0.50 eV and 0.73 eV for S_1 and S_1', respectively. This only slightly underestimates the experimental Stokes shifts of 0.64 and 0.87 eV.[22] This underestimation is likely an artifact of the functional used but may also be attributed to experimental factors such as solvent effects, counter ions, or intermolecular interactions. Some of these factors may be examined theoretically using solvent corrections or running dynamics; however, that is outside the scope of this current work.

Figure 6. (A)Proposed scheme of the origin of the dual emission (ems) peaks in $Au_{14}Cd(S\text{-}Adm)_{12}$. (B) Simplified graphical image of the excitation/relaxation process in the first enantiomer of $Au_{14}Cd(S\text{-}Adm)_{12}$. The first emissive point occurs at 1.09 eV with a radiative lifetime of 1.00 μs and the second emissive point occurs at 0.86 eV with a radiative lifetime of 3.71 μs.

The average bond lengths are reported in table 2 for the ground state (S_0), first emissive geometry (S_1) and second emissive geometry (S_1'). The placement of the mono-dopant, Cd, in the core is involved in the PL mechanism as the Au-Cd bridging bond guides the structural change responsible for the second emissive peak. Excitation to S_1 from the S_0 state leads to a large change in the core where the Au-Cd bond grows up to 0.16 Å. This bond continues to enlarge by more than 0.1 Å upon conversion from the S_1 to S_1' minima as seen in figure 7. We do see the same restrained type of behavior the experiments predicted between the emission peaks; however, overall, the core shape changes very little as the average Au-Au bond lengths in the core only vary by 0.007 Å. In addition, the Cd placement distorts the terminal bond on the tetrametric motif structure, giving large structural differences in the S-Au-S staple bonds. The length of the S-S staple that defines the motif structure becomes larger upon excitation from $S_0 \rightarrow S_1$ by 0.017 Å and shorter upon the conversion from $S_1 \rightarrow S_1$' by 0.057 Å.

There are additional differences between the two minima. Between S_1 and S_1', the HOMO level increases in energy from -4.14 eV to -4.07 eV and the LUMO level decreases in energy from -3.15 eV to -3.28 eV (figure S5). This decreases the HOMO-LUMO gap from 0.99 eV to 0.79 eV for the conversion from S_1 to S_1'. The orbitals themselves also look different. The HOMO and LUMO orbitals are essentially identical for S_0 and S_1, but upon conversion, the S_1' HOMO orbital differs. The S_1 HOMO has primarily superatomic P nature, while the HOMO from S_1' does not have a superatomic nature, and instead the major contributor to this orbital is the d atomic orbitals from the gold atoms. The LUMO orbitals are much more similar, with large s contributions from Cd, sp contributions from gold, and p contributions from the sulfur atoms.

Figure 7. Bond changes during excitation or conversion. The blue/pink solid lines represent the specific bond enlarging, while the red/orange dotted lines represent the specific bond shortening.

Average Bond Length (Å)			
Bond	**S_0**	**S_1**	**S_1'**
Au core - Au core	2.760 ± 0.076	2.753 ± 0.089	2.780 ± 0.098
Au shell - Au shell	2.941 ± 0.101	2.901 ± 0.079	2.855 ± 0.102
Au core - Cd core	2.833 ± 0.063	2.896 ± 0.109	2.949 ± 0.147
Au shell - S terminal	2.469 ± 0.021	2.471 ± 0.016	2.514 ± 0.069
Cd core - S terminal	2.530 ± 0.000	2.592 ± 0.000	2.594 ± 0.000
Au shell - S staple	2.401 ± 0.035	2.414 ± 0.040	2.429 ± 0.048
S staple - S staple	4.739 ± 0.037	4.756 ± 0.024	4.710 ± 0.081

Table 2. Average bond lengths of the ground state and both emissive geometries in $Au_{14}Cd(S\text{-}Adm)_{12}$ at the Xalpha/DZ level of theory.

The radiative lifetimes of S_1 and S_1' are found to be 1.00 μs and 3.71 μs, respectively. The theoretical radiative lifetime of the two emissive minima are calculated using equation 1 by the ADF program[2]

$$\frac{1}{\tau} = \frac{4}{3t_0} a_0^3 (\Delta E)^3 \sum_{\alpha \epsilon (x,y,z)} |M_\alpha|^2 \qquad (1)$$

where τ is the radiative lifetime, α_0 is the fine structure constant, ΔE is the vertical excitation energy, and M_α is the transition dipole moment in the $\alpha = x,y,z$ direction. The experiments find a dominant lifetime decay of 334 ps from the second emissive peak but are not able to distinctly fit the decay of the first emissive peak due to the overlap of the two excited-state absorptions.[22] The theoretical radiative lifetime value does not account for nonradiative transitions and dynamics between the emission peaks; hence, it cannot be directly compared to the experimental results. We can however conclude that the S_1’ minimum emits with a longer lifetime than the S_1 and both S_1 structures are predicted to have microsecond radiative lifetimes.

Conclusion:

The photoluminescent mechanism for $Au_{14}Cd(S\text{-}Adm)_{12}$ was analyzed using TDDFT gradients. The results show that dual emission is present and originates from two minimum points on the first electronically excited state, emitting 0.23 eV apart. The first emissive point was accessed via excitation to the S_1 state from the optimized ground state geometry, while the second emissive point was accessed via excitation to the S_2 state, followed by additional relaxation from the S_2 to the S_1. The average geometric differences between the minimum structures are quite large, which is a result from the Au-Cd ‘bridging’ bond enlarging more than 0.10 Å upon both excitation to the S_1 state (from S_0) and conversion to the S_1’ minimum (as measured from S_1). Both S_1 and S_1’ originate from the P → D superatomic orbitals due to the prominent HOMO-LUMO excitation in the core, demonstrating that the PL mechanism arises from emission between these core-based orbitals. Both lifetimes are predicted to lie in the microsecond timescale, which are long lifetimes for a singlet state. As dual emission is relatively rare, this paper serves as a theoretical basis for understanding the dual emission phenomenon in small emissive gold nanoclusters.

Supplementary Material:

See Supplementary Material for an optical absorption comparison between TDDFT and TDDFT+TB, a summary of the theoretical photoluminescence of the second enantiomer of $Au_{14}Cd(S\text{-}Adm)_{12}$, and coordinates of the S_0, S_1, and S_1’ optimized geometries for both enantiomers.

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Data Availability Statement:

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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