# First Principles Studies of Two Luminescent Molecular Quantum Clusters of Silver, Ag<sub>7</sub>(H<sub>2</sub>MSA)<sub>7</sub> and Ag<sub>8</sub>(H<sub>2</sub>MSA)<sub>8</sub>, Based on Experimental Fluorescence Spectra

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# ABSTRACT:

We report a joint experimental and theoretical study of two luminescent molecular quantum clusters of silver,  $Ag_7(H_2MSA)_7$  and  $Ag_8(H_2MSA)_8$  ( $H_2MSA$ ) ( $H_2$ 

# INTRODUCTION

Noble metal quantum clusters (QCs) showing confinement in their absorption profiles are fascinating materials of intense research today, in the fields of chemistry, biology, and materials science due to their novel size-dependent electronic and optical properties such as photoluminescence,<sup>1-3</sup> ferromagnetism,<sup>4</sup> optical chirality,<sup>5</sup> etc. Those properties make them good candidates for applications in catalysis,<sup>6,7</sup> nanoelectronics,<sup>8</sup> sensing,<sup>9,10</sup> and bioanalysis.<sup>11</sup> QCs of gold are particularly well-studied due to their extraordinary chemical stability as well as rich variety in optical properties. These clusters are also well studied theoretically due to the availability of more experimental data. However, commensurate expansion has not happened in the area of silver QCs. Silver nanoparticles have attracted considerable research interest due to their properties which are strongly correlated to the particles size,<sup>12–14</sup> shape,<sup>15,16</sup> surrounding environments,<sup>17</sup> and aggregation state.<sup>16</sup> Studies have shown that small silver clusters (up to about 8 atoms) have molecule-like optical transitions with absorption bands which depend on the number of constituent atoms and have bright fluorescence emission,<sup>18,19</sup> and clusters of up to 21 atoms exhibit one or more photoabsorption maxima.<sup>20</sup>

There have been several examples of template-assisted synthesis of water-soluble, highly luminescent  $Ag_n$  (n = 2-8) clusters.<sup>21–27</sup> However, there are only limited efforts in the case of

monolayer protected analogues, which include the synthesis of thiolate protected silver QCs.<sup>28–36</sup> For silver clusters, synthesis of water-soluble luminescent silver clusters with cores ranging from Ag<sub>2</sub> to Ag<sub>8</sub> have shown characteristic electronic transitions between 400–600 nm.<sup>21–27</sup> Silver clusters protected with aryl,<sup>28,29</sup> aliphatic,<sup>30,35,36</sup> and chiral<sup>31–34</sup> thiols have been reported, some of which have characteristic optical<sup>29,30,33</sup> and mass spectrometric<sup>28,30,33</sup> signatures.

Recently, Rao and Pradeep<sup>35</sup> have synthesized two new watersoluble luminescent silver clusters, protected by small molecules containing thiol groups, with well-defined molecular formulas,  $Ag_8(H_2MSA)_8$  and  $Ag_7(H_2MSA)_7$ , respectively. According to experimental results, the observed luminescence of  $Ag_8$  exhibits a strong dependence on temperature and solvent. The temperature sensitivity of the emission suggests a range of applications for this material. Their results also provide basic guidelines for further experimental and theoretical studies on the geometric and electronic structures, as well as photophysical properties of these clusters. Motivated by their experiments, we focus our present work on determining possible structures theoretically and

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elucidating the observed luminescence of these two clusters by performing density functional calculations.

# EXPERIMENTAL SECTION

Synthesis Procedure. Ag7 and Ag8 were synthesized as described before.<sup>35</sup> Confirmation of the molecular formulas came from mass spectrometric studies with soft ionization techniques such as electrospray ionization (ESI) and matrix-assisted laser desorption ionization (MALDI). First, Ag@(H<sub>2</sub>MSA) nanoparticles of 5-10 nm size were synthesized by the reported method.<sup>35</sup> They were subjected to interfacial etching in an aqueous/ organic biphasic system. H<sub>2</sub>MSA thiol was partially dissolved in an organic solvent and parent  $Ag@(H_2MSA)$  was dispersed in the aqueous phase. An aqueous solution of the as-synthesized  $Ag@(H_2MSA)$  nanoparticles was added to an excess of  $H_2MSA$ in toluene (1/2 water/toluene ratio). A weight ratio of 1:3 was used  $(Ag@(H_2MSA):H_2MSA)$ . The resulting mixture was stirred for 48 h at room temperature. Initiation of interfacial etching is indicated by the appearance of a blue layer at the interface after 0.5-1 h. As the reaction proceeds, the color of the aqueous phase changes from reddish brown to yellow and finally to orange.

**Instrumentation.** Perkin-Elmer Lambda 25 UV—vis spectrometer was used for UV—vis spectral measurements. Spectra were typically measured in the range of 190—1100 nm. Luminescence measurements were carried out using a HORIBA JOBIN VYON Nano Log instrument. The band-pass for excitation and emission was set as 5 nm. Transmission electron microscopy (TEM) images were collected using a JEOL 3010 microscope. A diluted solution was spotted on a carbon-coated copper grid and was dried under ambient conditions. Images were collected at 200 keV, to reduce beam induced damage of the clusters. Our earlier studies had shown that small clusters are highly sensitive to electron beams and coalesce to yield nanoparticles on the grid.

**Observations.** During the interfacial etching, the optical absorption spectrum of metallic silver nanoparticles showed gradual disappearance of the surface plasmon resonance at 400 nm. A new optical feature is obtained at 550 nm after 48 h of the reaction. It is known that, as the size of the silver nanoparticles approaches the de Broglie wavelength of the conduction electrons ( $\sim 1$  nm), the quasicontinuous electronic bands evolve to discrete levels. The absence of the peak at 400 nm and the emergence of one at 550 nm indicates that the size of the parent silver nanoparticles is clearly reduced below the fermi wavelength of the silver, so that the plasmon band at 400 nm disappears and discrete energy levels appear. In accordance with the previous studies of silver clusters, we assign this peak to interband transitions between orbitals derived from the 4d valence band and 5sp conduction band. Templated  $Ag_n$  clusters<sup>21–27</sup> and monolayer-protected clusters  $^{28-34}$  show interband transitions between 400 and 600 nm. The reduction in size during etching was clearly seen in TEM. The orange powder separated from the aqueous phase after 48 h of etching exhibits red emission in the solid and solution states. This crude mixture was subjected to polyacrylamide gel electrophoresis (PAGE) to achieve the separation of Ag<sub>7</sub> and Ag<sub>8</sub> clusters. The first band due to Ag<sub>8</sub>(H<sub>2</sub>MSA)<sub>8</sub> was red in color and the second band due to  $Ag_7(H_2MSA)_8$  was light yellow in visible light. The bands are, however, seen clearly in the UV; Ag<sub>8</sub> is pink at 0 °C and Ag<sub>7</sub> is blue-green at room temperature. These bands were separated and the free clusters were collected in water. Ag<sub>8</sub>(H<sub>2</sub>MSA)<sub>8</sub> has a characteristic optical absorption



Figure 1. UV/vis and luminescence spectra of Ag<sub>8</sub>(H<sub>2</sub>MSA)<sub>8</sub> clusters obtained from the first band in PAGE. The cluster in water was excited at 550 nm and emission observed at 650 nm. Inset shows a photographs of aqueous solution of Ag<sub>8</sub>(H<sub>2</sub>MSA)<sub>8</sub> under a UV lamp at 0 °C.



**Figure 2.** UV/vis and luminescence spectra of  $Ag_7(H_2MSA)_7$  obtained from the second band in PAGE. The cluster in water was excited at 350 nm, and emission was observed at 440 nm. Inset shows a photograph of aqueous solution of  $Ag_7(H_2MSA)_7$  under a UV lamp at 25 °C.

signature at 550 nm, in agreement with that of the crude product. The luminescence spectrum of  $Ag_8(H_2MSA)_8$  shows an excitation maximum at 550 and emission maximum at 650 nm (Figure 1). The quantum yield calculated for  $Ag_8(H_2MSA)_8$  in water at room temperature is 0.3%. It is known that the enhancement in emission even with a small decrease in temperature is significant, and this enabled photographing the solutions at lower temperatures (Figure 1). A very large enhancement of this kind in a narrow temperature window is interesting and may result in a range of applications for this material.

The optical absorption spectrum of  $Ag_7(H_2MSA)_7$  has no distinguishable feature in the visible region.  $Ag_7(H_2MSA)_7$  emits observable blue—green luminescence at room temperature (Figure 2). The quantum yield calculated for  $Ag_7(H_2MSA)_7$  in water at room temperature is 5%. The luminescence spectrum of  $Ag_7$ - $(H_2MSA)_7$  shows an excitation maximum at 350 nm and emission maximum at 440 nm (Figure 2). Excitation and emission spectra of both of these clusters  $(Ag_8(H_2MSA)_8 \text{ and } Ag_7(H_2MSA)_7)$  were retained even after phase transfer to toluene using a tetraoctyl ammonium bromide (TOABr).

Luminescence decays of  $Ag_8$ , in the solid state and  $Ag_7$  in the liquid state were measured using two facilities. The data obtained using a picosecond time correlated single photon counting (TCSPC) technique as shown in a previous report.<sup>35</sup> Life time values of  $Ag_8$  clusters were obtained by numerical fitting of the emission at 630 nm. The luminescence decay profile showed four components at 35 ps (97%), 37.2 ns (0.6%), 37.2 ns (1.72%), 0.53 ns (1.72%), and 5.68 ns (0.6%), respectively. Life time values of  $Ag_7$  were obtained by the numerical fitting of the emission at 440 nm. Luminescence decay profile showed four components at 0.012 ns (88.9%), 0.396 ns (4.8%), 2.10 ns (4.8%), and 8.31 ns (1.3%), respectively. Both the clusters show a dominant fast component.

## COMPUTATIONAL METHODS

All of the computations were carried out with relativistic effective core potentials (RECP) that kept the outer valence  $4d^{10}5s^1$  shells of silver atom,  $2s^22p^2$  for carbon atom, and  $3s^2$   $3p^4$  for sulfur atom, replacing the rest of the electrons by RECPs. The basis sets compatible with these RECPs were taken from Ross et al.<sup>37</sup>

The putative GMs (global minima) for singlet state Ag<sub>7</sub> and Ag<sub>8</sub> were obtained by global optimization with no a priori assumption about the structures. The calculations combined the Taboo Search in Descriptor Space (TSDS) global optimization method<sup>38</sup> with the energy evaluated with the Gaussian 09 software<sup>39</sup> using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation (XC) functional.<sup>40</sup> In our global search run, we have about 500 energy evaluations, and the best 15 structures were selected for local optimization, which took about 50-60 steps to converge. So, it required about 1400 energy evaluations to get the best low energy candidates. After obtaining the optimized ground state isomers, we performed single point calculations using PBE by the Gaussian 09 software for triplet states based on the structures of the ground states. The absorption spectra were simulated by calculating the oscillator strengths within time-dependent density functional theory (TDDFT).

It is worth to mention that we carried out DFT calculations for  $Ag_n(SCH_3)_n$  (n = 7, 8), which is a theoretical model for  $Ag_n(H_2MSA)_n$  (n = 7, 8). Such a simplification of ligands was frequently used in the previous studies<sup>41–47</sup> in order to avoid incredibly large computational costs. Furthermore, Iwasa and Nobusada's study<sup>46</sup> confirmed the effectiveness of the simplification based on the fact that experimental absorption spectrum of  $Au_{25}(SL)_{18}$  has a lack of dependence on the ligand L. According to previous studies mentioned above, we adopted the simplification of ligands in our calculations and discussions.

# RESULTS AND DISCUSSION

**Geometry.** Here we briefly summarize the lowest energy structures of  $Ag_7$  and  $Ag_8$ . (a) For  $Ag_7$ , the  $D_5$  h structure was found to be most stable among all isomers by the equation-of-motion coupled cluster singles and doubles (EOM-CCSD) method and DFT-BLYP (density functional theory with Becke exchange functional, and Lee-Yang-Parr correlation functional),<sup>48</sup> while the  $C_{3\nu}$  structures were 0.36 and 0.31 eV above on the potential energy surface, respectively. Harb et al.<sup>49</sup> also found  $D_{5h}$  to be most stable using DFT-BP86 (density functional theory with Becke exchange functional and Perdew86 correlation functional).

Table 1.	Core St	tructures	of Ag <sub>7</sub>	and Ag <sub>8</sub>	3 Obtained	from a
Global Se	earch					

$Ag_7$	Spin	T <sub>e_pbe</sub>	R <sub>nn</sub>
	state	(eV)	(angstrom)
	Singlet	0	3.01
	Triplet	1.11	
	Singlet	0.11	3.00
	Triplet	1.99	
(2)			
Ag <sub>8</sub>	Spin state	T <sub>e_pbe</sub> (eV)	R <sub>nn</sub> (angstrom)
Ag <sub>8</sub>	Spin state Singlet	T <sub>e_pbe</sub> (eV) 0	R <sub>nn</sub> (angstrom) 2.99
Ag <sub>8</sub>	Spin state Singlet Triplet	Т <sub>е_рье</sub> (eV) 0 1.72	R <sub>nn</sub> (angstrom) 2.99
Ag <sub>8</sub> (1)	Spin state Singlet Triplet Singlet	Te_pbe           (eV)           0           1.72           0.06	R <sub>nn</sub> (angstrom) 2.99 3.00
Ag <sub>8</sub> (1)	Spin state Singlet Triplet Singlet Triplet	Te_pbe           (eV)           0           1.72           0.06           1.97	R <sub>nn</sub> (angstrom) 2.99 3.00

Table 2. Optimized  $Ag_7(SCH_3)_7$  and  $Ag_8(SCH_3)_8$  Isomers with Geometric Parameters and Energies

Ag <sub>7</sub> (SCH <sub>3</sub> ) <sub>7</sub> (1)		R_Ag-Ag	R_s-Ag	R_C-H	$\mathbf{R}_{s-c}$	T <sub>e</sub>
	Singlet	3.27-4.10	2.59-2.71	1.10	( <b>A</b> ) 1.92-1.94	0
	Triplet					2.56
Ag <sub>7</sub> (SCH <sub>3</sub> ) <sub>7</sub> (2)		R_Ag-Ag (Å)	R_s-Ag (Å)	R_с-н (Å)	R_s-c (Å)	T <sub>e</sub> (eV)
	Singlet	3.17-4.09	2.60-2.78	1.10	1.91-1.93	0.08
	Triplet					2.48
Ag <sub>8</sub> (SCH <sub>3</sub> ) <sub>8</sub> (1)		R_Ag-Ag (Å)	R_s-Ag (Å)	R_C-H (Å)	R_s-c (Å)	T <sub>e</sub> (eV)
Ag <sub>8</sub> (SCH <sub>3</sub> ) <sub>8</sub> (1)	Singlet	R_Ag-Ag (Å) 3.20-4.02	R_s-Ag (Å) 2.59-2.77	<b>R_</b> с-н (Å) 1.10	R_s-c (Å) 1.91-1.93	<b>T</b> e (eV) 0
Ag <sub>8</sub> (SCH <sub>3</sub> ) <sub>8</sub> (1)	Singlet Triplet	R_Ag-Ag (Å) 3.20-4.02	R_s-Ag (Å) 2.59-2.77	R_C-H (Å) 1.10	R_s-c (Å) 1.91-1.93	Te           (eV)           0           2.54
Ag <sub>8</sub> (SCH <sub>3</sub> ) <sub>8</sub> (1)	Singlet Triplet	R_Ag-Ag (Å) 3.20-4.02 R_Ag-Ag (Å)	R_S-Ag (Å) 2.59-2.77 R_S-Ag (Å)	<b>R</b> _С-н (Å) 1.10 <b>R</b> _С-н (Å)	R_s-c (Å) 1.91-1.93 R_s-c (Å)	Te (eV) 0 2.54 Te (eV)
Ag <sub>8</sub> (SCH <sub>3</sub> ) <sub>8</sub> (1)	Singlet Triplet Singlet	R_Ag-Ag (Å) 3.20-4.02 R_Ag-Ag (Å) 3.14-3.84	R_s-Ag (Å) 2.59-2.77 R_s-Ag (Å) 2.59-2.79	R_C-H         (Å)           1.10	R_s-c (Å) 1.91-1.93 R_s-c (Å) 1.91-1.93	Te           (eV)           0           2.54           Te           (eV)           0.43

Besides, studies using tight-binding molecular dynamics (TBMD),<sup>50</sup> DFT-LSD (density functional theory with local spin-density approximation)<sup>51</sup> and many-body perturbation theory (MBPT)<sup>52</sup>

also indicate the  $D_{5h}$  pentagonal structure to be the most stable among all the isomers. (b) For Ag<sub>8</sub>, the  $T_d$  structure was found to be most stable among all the isomers by the equation-of-motion coupled cluster singles and doubles (EOM-CCSD) method and DFT-BLYP (density functional theory with Becke exchange functional, and Lee-Yang-Parr correlation functional),<sup>48</sup> whereas the  $D_{2d}$  structures were 0.10 and 0.09 eV higher in energy respectively. Similarly, Harb et al.<sup>49</sup> found that  $D_{2d}$  was 0.04 eV higher in energy than  $T_d$ . Tight-binding molecular dynamics (TBMD)<sup>50</sup> predicted the  $D_{2d}$  structure to be lowest in energy while DFT-LSD (density functional theory with local spin-density approximation)<sup>51</sup> and many-body perturbation theory (MBPT)<sup>52</sup> gave the result that the  $D_{2d}$  structures were 0.12 and 0.10 eV below the  $T_d$  structures on the potential energy surface, respectively.

Our global search results for core structures of Ag<sub>7</sub> and Ag<sub>8</sub> are summarized in Table 1. For Ag<sub>7</sub>, the  $D_{5h}$  is lowest in energy and  $C_{3\nu}$  is 0.11 eV higher, whereas for Ag<sub>8</sub>, the  $D_{2d}$  structure is lowest in energy and the  $T_d$  lies 0.06 eV above on the PES (potential energy surface). We construct the initial Ag<sub>7</sub>(SCH<sub>3</sub>)<sub>7</sub> and Ag<sub>8</sub>-(SCH<sub>3</sub>)<sub>8</sub> isomers by passivating methanethiolate to core Ag<sub>7</sub> and Ag<sub>8</sub> structures from Table 1, and perform local optimizations to get the optimized structures of  $Ag_7(SCH_3)_7$  and  $Ag_8(SCH_3)_8$ . After the local optimization, single-point calculations are carried out based on the optimized singlet structures to get the energy for the vertical triplet states. The geometries and detailed bond lengths of the two lowest energy structures [(1) corresponds to the lowest energy structure and (2) corresponds to the second lowest energy structure as indicated in Table 2 and Figures 3 and 5] for  $Ag_7(SCH_3)_7$  and  $Ag_8(SCH_3)_8$  are shown in Figure 3, whereas the energy of the ground state, triplet state, and general structural parameters are summarized in Table 2. For all of the isomers in Table 2, the lowest vibrational frequencies have been checked to be positive in order to make sure that they are local minima.

In previous studies of thiolate-protected gold nanoclusters, two types of "stable" motifs, the simple motif -RS-Au-RSand the extended motif -RS-Au-RS-Au-RS- have been discovered to enhance the stability of the clusters.<sup>53-56</sup> In the case of silver, Xiang et al. proposed a new structure of  $[Ag_7(DMSA)_4]^$ with -RS-Ag-RS- as a stable motif in a thiolate-protected Ag cluster in their recent paper.<sup>57</sup> Considering the possibility of -RS-Ag-RS- working as a stable motif for our  $Ag_7(SCH_3)_7$ 



Figure 3. Continued



**Figure 3.** (a) Optimized structure of  $Ag_7(SCH_3)_7$  (1) from Table 2 before and after optimization. The Ag-S bond lengths are indicated in blue, whereas Ag-Ag bond lengths are in black. (b) Optimized structure of  $Ag_7(SCH_3)_7$  (2) from Table 2 before and after optimization. (c) Optimized structure of  $Ag_8(SCH_3)_8$  (1) from Table 2 before and after optimization. (d) Optimized structure of  $Ag_8(SCH_3)_8$  (2) from Table 2 before and after optimization.

and  $Ag_8(SCH_3)_{8}$ , we constructed the initial structure with -RS-Ag-RS- for  $Ag_7(SCH_3)_7$  and  $Ag_8(SCH_3)_8$ , besides the ones with -RS-Ag-, and carried out local optimizations for both of them. The results show that, no matter which type of thiolatepassivating (-RS-Ag-RS- or -RS-Ag-) structure we choose in the beginning of optimization, the final optimized structures always resulted in the more stable -RS-Ag-RS- structure as shown in Figure 3. For example, the initial structure of Ag<sub>7</sub>- $(SCH_3)_7(1)$  is constructed with the -RS-Ag-RS- motif, and the optimized structure converged to a thiolate-protected one with -RS-Ag-RS-. For other structures in Figure 3, even if we start with initial structures of -RS-Ag-, the structures still converged to local minima with -RS-Ag-RS- as the stable motif. Compared to the Au core of the thiolate-protected Au<sub>102</sub>- $(p-MBA)_{44}$   $(p-MBA = SC_7O_2H_5)^{47}$  and  $Au_{25}(SR)_{18}^{-54-56}$  the optimized structures in Figure 3 are commonly deformed compared to the corresponding initial structures due to the small

size of the core silver cluster, which is similar to the case of  $[Ag_7(DMSA)_4]^-$  in that its final optimized chiral structure originates from an initial 2-dimensional structure.<sup>51</sup>

It should be noted that the  $-SCH_3$  ligands maintained the basic structure with no bond breaking after the optimizations. Furthermore, we generated the infrared spectrum of  $Ag_7(SCH_3)_7$  (1) in Figure 4, which has features matching well with the experimental results of hydrocarbon chains in the solid state thiolate-protected silver clusters,<sup>58</sup> such as C–S stretching at 615 cm<sup>-1</sup>, which generally agrees with the experimental value<sup>58</sup> 600 cm<sup>-1</sup>, a C–H symmetric and antisymmetric stretching at 2794 and 2810 cm<sup>-1</sup> which generally matches the experimental C–H stretching region<sup>58</sup> showing characteristic features at 2849 and 2916 cm<sup>-1</sup>. On the basis of this information, we have omitted the –CH<sub>3</sub> groups in the structures shown in Figure 3 in order to reduce the complexity of the figure, and we have added dashed lines for distances longer than 4.20 Å between certain atoms for

the optimized structures in order to make connections to their corresponding initial structures visually.

**Electronic Properties.** As can be seen from the discussion above, deformations of the silver core structures are common and are caused by the interaction between silver atoms and sulfur atoms of the methanethiolates. To further understand this inter-



**Figure 4.** Infrared spectrum of  $Ag_7(SCH_3)_7$  (1) ( $\nu$  denotes the vibrational modes).

action, the Mulliken populations were analyzed to obtain the amount of charge transfer from silver to sulfur. The values thus obtained for  $Ag_7(SCH_3)_7(1)$  are Ag (0.27) and S (-0.27); for  $Ag_7(SCH_3)_7(2)$ , Ag (0.28) and S (-0.28); for  $Ag_8(SCH_3)_8(1)$  Ag (0.26) and S (-0.27); and for  $Ag_8(SCH_3)_8(2)$  Ag (0.26) and S (-0.27). Therefore, on an average, the Ag-S bond distance (shown in Table 2) becomes rather small compared to the Ag-Ag bond distance, which is much larger than that in a bare silver cluster (Table 1). Also, the HOMO-LUMO gaps were increased by attaching ligands, i.e., from 0.34 to 2.44 eV for  $Ag_7(SCH_3)_7(1)$ , from 0.36 to 2.27 eV for  $Ag_7(SCH_3)_7(2)$ , from 1.77 to 2.41 eV for  $Ag_8(SCH_3)_8(1)$ , and from 2.04 to 2.05 eV for  $Ag_8(SCH_3)_8(2)$ . Consequently, as expected, the methanethiolates stabilize the bare silver cluster through the formation of the -RS-Ag-RS- bonds.

**Excitation Spectra.** According to the experimental results mentioned in the Experimental Section, the emission spectra (Figure 2) of clusters 1 ( $Ag_8(H_2MSA)_8$ ) and 2 ( $Ag_7(H_2MSA)_7$ ) show sharp maxima at 650 (1.91 eV) and 440 nm (2.82 eV), with excitation maxima of 550 (2.25 eV) and 350 nm (3.54 eV), respectively. Fluorescence is a process in which a fluorophore absorbs light of a particular wavelength and then emits a quantum of light that corresponds to the energy difference between the excited and ground states. Consequently, the fluorescence spectrum of excitation maxima and emission maxima correlates first



Figure 5. (a) Simulated excitation spectra of  $Ag_7(SCH_3)_7(1)$  and (2) (top to bottom). (b) Simulated excitation spectra of  $Ag_8(SCH_3)_8(1)$  and (2) (top to bottom).

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with an excitation to an excited state above the ground state, followed by an emission to a triplet state above ground state. Those maxima provide guidelines for our theoretical investigations of simulated excitation spectra using TDDFT methods and they are marked as reference points on the spectra in Figure5.

As it is shown in Figure 5, panels a and b, the theoretical spectra of  $Ag_7(SCH_3)_7$  and  $Ag_8(SCH_3)_8$  generally agree quite well with the experiments. The triplet states are obtained from single point calculation based on the optimized singlet structures, so we would expect these vertical triplet states to be higher in energy than the optimized triplet states. For two  $Ag_7(SCH_3)_7$ isomers (Figure 5a), the calculated triplet state lies within 0.2 eV of the experimental value of 2.82 eV, and there exist several excited states with relatively strong oscillator strengths coinciding with the experimentally measured value of 3.54 eV. For two  $Ag_8(SCH_3)_8$  isomers (Figure 5b), the calculated triplet state for isomer 1 is 0.62 eV higher than the experimental value of 1.91 eV, whereas the triplet state for isomer 2 is 0.37 eV higher than the experimental result. It is thus possible that the experimental results correspond to optimized triplets which lie in lower energy region of the potential energy surface. For both the isomers, there are also several excited states with relatively strong oscillator strengths located reasonably close to the experimentally measured value of 2.25 eV.

From the experimental standpoint, it could be hard to identify triplet states from excited states as relativistic effects of the silver atom are large enough and thus owing to the spin—orbit splitting of Ag triplet-singlet mixing is feasible. Thus excited states lower than the triplet state are feasible for these silver clusters as a result of spin—orbit splitting. As shown in Figure 5, the lower energy region of two  $Ag_7(SCH_3)_7$  isomers could be formed on the basis of this reasoning. We use two different designations, "triplet" and "excited states" for convenience to distinguish them in our discussion of theoretical results.

On the whole, by considering coexistence of isomers owing to small energy differences between isomers, the theoretically simulated spectra provided sufficient information on excited states with relatively strong oscillator strengths in the excitation and emission regions of the observed spectra, and illustrated that the dominant fast components (88.9% of 0.012 ns for Ag<sub>7</sub> and 97% of 35 ps for Ag<sub>8</sub>) in emission from the luminescence decay profile correspond to the decay from the first excited state to the triplet state. Furthermore, good agreement of the simulated excitation spectra with experimentally observed peaks confirms the possible existence of our optimized structures in the experimental conditions.

# CONCLUSION

Guided by experimental results of fluorescence spectroscopy, we have carried out a first principles study of two luminescent molecular quantum clusters,  $Ag_7(H_2MSA)_7$  and  $Ag_8(H_2MSA)_8$ . Agreement between theoretical and experimental excitation spectra confirms the structural properties of the clusters, especially the existence of -RS-Ag-RS- as a stable motif for thiolate-protected silver clusters. The correlation between experimental and theoretical geometric and electronic structure information may lead to a fundamental understanding of the factors affecting stabilization of thiolate-protected nanoclusters and exploring applications related to the temperature sensitivity of emission.

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