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# Fluorescence enhancement of DHLA protected gold nanoclusters in the presence of salt

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A new method for enhancement of fluorescence for DHLA protected gold nanoclusters has been proposed by the assistance of sodium citrate salt. The mechanism for the enhancement has been investigated. Furthermore, DHLA protected gold nanoclusters have been investigated in the presence of several other kinds of salts. The influences for the fluorescence behaviours by various kinds of salt have also been summarized.

## 1 Introduction

Nobel metal nanoclusters have received great attentions due to their ultra-small size, electronic, optical, fluorescent, and biocompatible properties.<sup>1-5</sup> Among the properties, the fluorescence behaviours have attracted great attentions.<sup>2, 6-8</sup> The syntheses of nanoclusters with brighter fluorescence are promising for applications in various fields. Thus, efforts have been paid over the last years in improving the fluorescence of nanoclusters.<sup>6, 9-11</sup> For example, microwave assisted methods have shed light on the improvement of the quantum yield for the fluorescence of gold nanoclusters (Au NCs).<sup>12</sup> However, the method is still not available in some basic laboratory for undergraduates. Another example for improvement of fluorescence is through the phase transfer process. Yuan developed an electrostatically induced reversible phase transfer process that enabled originally non-fluorescent silver nanoclusters (Ag NCs) into highly fluorescent Ag NCs.<sup>13</sup> Notwithstanding, the involvement of toxic phase transfer materials such as Tetramethylammonium hydroxide (TMAH) is not favourable for further application. The same group also developed a desalting column process to improve thiolate Ag NCs from non-fluorescent to highly fluorescent nanoclusters.<sup>14</sup> Though they stated that Ag NCs describe bright fluorescence after the separation by the column, but the procedure is complicate to operate.

Recently, the aggregation-induced method<sup>15</sup> has been developed for the fluorescence enhancement. For instance, Luo found a simple strategy to induce the aggregation of Au(I)-thiolate complexes, which in-situ generated Au(0) cores to form Au(0)@Au(I)-thiolate core-shell NCs.<sup>16</sup> The fluorescence was greatly enhanced due to the aggregation. As well as this, Jia developed highly fluorescent copper nanoclusters (Cu NCs) with a quantum yield of 16.6% that displayed an intriguing aggregation-induced emission.<sup>17</sup> Though the aggregation of nanoclusters significantly improves the brightness of the fluorescence for Au NCs and Cu NCs at some conditions, these aggregates are no longer soluble in water, which will limit their applications in aqueous system.

There still exist some disadvantages for previous methods. Thus the development of simpler, cost effective and water soluble methods for enhancement of the fluorescence are still in requirement. It is reported that the ligand may play an important role for the fluorescence behaviour of Au NCs.<sup>18</sup> Thus, it may be promising to make the best of the ligand to improve the fluorescence intensity. In this work, we try to signify the effect of a thiolate ligand to modify the fluorescence of Au NCs. It is well know that the addition of salt will inhibit the repulsion of charges on the gold core. Therefore, higher concentrations of NaCl salt were previously reported to result in higher SH-DNA (Thiol modified DNA) loading on gold core of nanoparticles according to the papers.<sup>19-21</sup> Then, similar to the loading of thiol (-SH) modified DNA on gold core of nanoparticles, higher concentration of salt will maximize the loading of Dihydrolipoic acid (DHLA) on gold core of nanoclusters because DHLA features a pair of -SH groups.

Enlightened by those phenomena, it is expected that the salt aging process during the synthesis of Au NCs could influence the fluorescence behaviour due to the modification of surface condition for gold core by DHLA.

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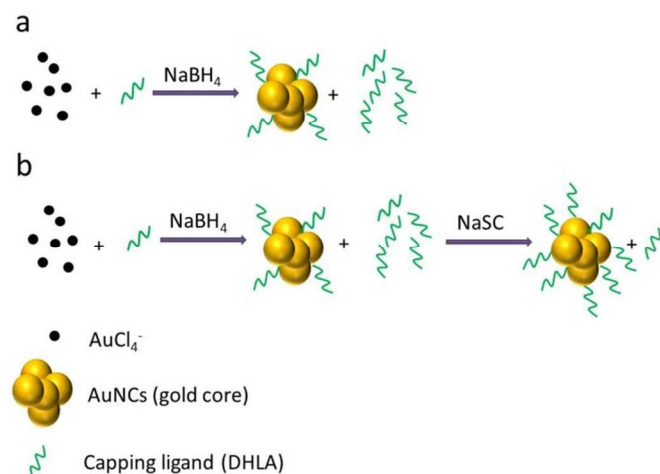
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Previous work has mentioned some nanoclusters are stable in salt media,<sup>22</sup> but the fluorescence enhancement in the presence of salt has never been reported to the best of our knowledge. In this work, a simple strategy for the employment of sodium citrate (NaSC) salt was proposed for the fluorescence enhancement of nanoclusters. We found that NaSC salt plays a crucial role in increasing the fluorescence of DHLA stabilized Au NCs (DHLA-Au NCs). A mechanism for the fluorescence enhancement process has been proposed in Scheme 1 based on the characterization such as DLS, TEM and fluorescence spectroscopy. Part a demonstrated a previously reported method for the formation of DHLA-Au NCs; Part b reveals that NaSC salt will induce more amounts of thiolate ligands adsorbing or binding on the gold core, which is similar to the modification of gold nanoparticle by thiol modified DNA.<sup>23</sup>



**Scheme 1** Schematic illustration of our proposed mechanism for the fluorescence enhancement of DHLA-Au NCs: a, formation of DHLA-Au NCs in the absence of salt; b, formation of DHLA-Au NCs in the presence of salt (NaSC).

## 2 Experimental

### Reagents and instruments

Sodium citrate tribasic dehydrate (>99%) (NaSC), Gold(III) chloride trihydrate (>99.9%) ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ), Sodium borohydride (98%) ( $\text{NaBH}_4$ ), Sodium hydroxide (>98%) ( $\text{NaOH}$ ) and ( $\pm$ )- $\alpha$ -Lipoic acid (>99%) were purchased from Sigma Aldrich. Other metal salts are of analytical grades and purchased from Sinopharm Group Company. All the materials for synthesis of DHLA-Au NCs were used as received without further purification. Deionized water was used through the experiment. Fluorescence spectra were recorded on a FS-2 spectrophotometer (SCINCO) with an excitation wavelength at 460 nm. Transmission electron microscope (TEM) images were obtained on a Hitachi transmission electron microscope using a JEM-1400 microscope (JEOL, Tokyo, Japan) operated at 120 kV. Absorption spectra were performed on a UV-visible spectrometer (UV-2600, Shimadzu, Japan). X-ray photoelectron spectroscopy (XPS) spectra were obtained on Escalab 250 X-ray photoelectron spectroscope. Dynamic Light Scattering

(DLS) measurement was performed on a Malvern Zetasizer (v2.2).

### Preparation of DHLA-Au NCs

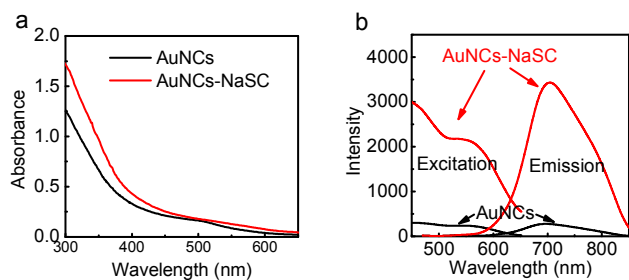
DHLA stabilized Au NCs was synthesized in aqueous solution following a similar synthetic route reported previously.<sup>24</sup> In a typical experiment, 5.2 mg of  $\alpha$ -lipoic acid was added to 16 ml of aqueous solution. After that, 50  $\mu\text{L}$  of  $\text{NaOH}$  (2.0 M) was combined to decompose  $\alpha$ -lipoic acid to DHLA. The mixture was stirred for several minutes until the solution became transparent, followed by addition of 320  $\mu\text{L}$  of  $\text{HAuCl}_4$  (1% by mass). Finally, an aqueous solution of  $\text{NaBH}_4$  (200  $\mu\text{L}$ , 0.1 M) was added slowly to the mixture under rapid stirring. The mixture was kept overnight.

### Preparation of DHLA-Au NCs in the presence of salt

The synthesis of DHLA-Au NCs in the presence of NaSC salt was followed a previous reported protocol.<sup>24</sup> However, after the addition of  $\text{NaBH}_4$ , 1.5 M of NaSC was added gradually. And then, the mixture was kept stirring for the same time as the preparation of DHLA-Au NCs. In the case of comparison for fluorescence enhancement, no further treatment was performed. For further application, the solution could be dialyzed with a 10 kDa cut-off dialysis bag against doubly distilled water for more than 24 hours with a water change every 4 h to remove the salt.

## 3 Results and discussion

It is expected that the synthesized DHLA-Au NCs exhibit molecule-like behaviour. Thus, the optical character for DHLA-Au NCs described different features compared to gold nanoparticles, see Fig. 1. As shown in Fig. 1a, DHLA-Au NCs solution prepared in the absence and presence of salt demonstrate comparable absorbance at 460 - 500 nm. This indicated there might be no significant difference between the concentrations of original DHLA-Au NCs and modified DHLA-Au NCs. Fig. 1b describes the corresponding fluorescence spectra. The maximum fluorescence excitation and emission wavelengths of DHLA-Au NCs are located at 460 nm and 705 nm respectively. The quantum yield is calculated as 2.9-3.1% using (Rhodamine 6G (QY = 0.95 in ethanol)) and Nile blue perchlorate (QY = 0.27 in acidic ethanol) as references. The as-prepared DHLA-Au NCs in the presence of NaSC salt exhibit ca. 10 times enhancement for the fluorescence intensity using original DHLA-Au NCs as a reference.

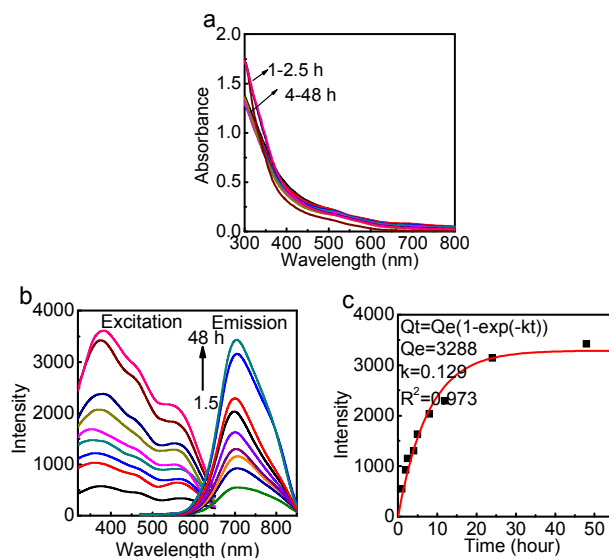


**Fig. 1** UV-vis (a) and fluorescence spectra (b) for DHLA-Au NCs prepared in the absence (black line) and presence of NaSC salt (1.5 M) (red line).

Modification of DHLA-Au NCs by the assistance of NaSC salt as a function of time has been investigated by UV-Vis and fluorescence measurements. The evolutions for UV-Vis and fluorescence spectra of DHLA-Au NCs are plotted in Fig. 2. It can be seen from Fig. 2a that the UV-vis spectra for Au NCs at 460 - 500 nm with and without the assistance of NaSC described similar absorbance. However, by the addition of NaSC, the fluorescence excitation and emission maximum intensities are significantly enhanced up to 48 hours, see Fig. 2b. Initially, Au NCs with weak fluorescence intensity are first obtained in the mixture due to the formation of similar DHLA-Au NCs to the previously reported paper.<sup>24</sup> Meanwhile, DHLA-Au NCs describe weak fluorescence until 24 hours without the addition of NaSC salt. Furthermore, it can be seen from Fig. 2c that the emission intensity increases as a function of time. The experimental results could be adjusted to the following equation:

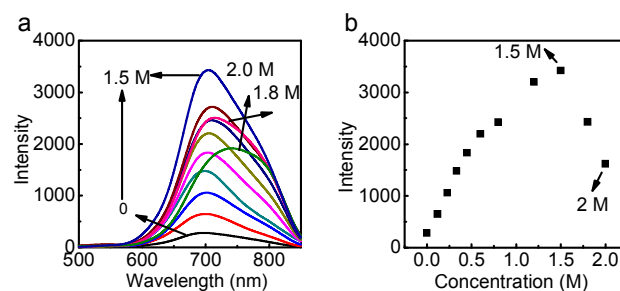
$$Q_t = Q_e(1 - \exp(-kt))$$

Where  $Q_t$  is the emission intensity,  $t$  is the evolution time and  $Q_e$  is the maxim intensity. This equation was used for homogeneous sorbents and physical sorption, which followed the Pseudo first order model.<sup>25</sup> Herein, it can be used to simulate the relationship between reaction time and intensity. It is concluded the increase of the fluorescence intensity is possibly caused by the adsorption of more amounts of DHLA ligands based on the well-fitting of the equation. Therefore it can be concluded that salt aging during the synthesis process improved the intensity of fluorescence, which was possibly facilitated by surface modification based on the adsorption of the thiolate ligand. However, after further extending the formation time, little increase for the fluorescence intensity was observed. This was possibly due to the coverage by higher density of capping ligands, which would cause the steric hindrance effect that inhibited further adsorption.



**Fig. 2** Time Evolution of UV-Vis (a), fluorescence spectra (b) and emission intensity for DHLA-Au NCs in the presence of 1.5 M of NaSC salt (c).

We also investigated the fluorescence of DHLA-Au NCs as a function of the concentration of NaSC salt, which were shown in Fig. 3. It can be seen from Fig. 3a that the fluorescence spectra describe sharp peaks from 0 to 1.5 M of NaSC. However, the spectrum describes a broad peak when NaSC is as high as 2.0 M, which indicates the partly aggregation of DHLA-Au NCs in the presence of high concentration of NaSC salt. It can be clearly observed from Fig. 3b that the fluorescence intensity gradually increased by the addition of 0 to 1.5 M of NaSC. After further increasing the concentrations of NaSC, the fluorescence spectra display lower intensities. This is probably caused by the formation of aggregates and bigger size nanoparticles. Thus, the results indicate the maxim concentration of NaSC is limit to 1.5 M for obtaining DHLA-Au NCs with excellent dispersity.



**Fig. 3** Fluorescence emission spectra (a) and the maxim emission intensity (b) as a function of the concentration of NaSC salt for DHLA-Au NCs.

TEM studies (Fig. 4) are used to investigate the size of DHLA-Au NCs in the absence (Fig. 4a), presence of 0.5 M (Fig. 4b), 1.5 M (Fig. 4c) and 2.0 M of NaSC (Fig. 4d). The size distribution diagrams and DLS measurements are

demonstrated in Fig. S1 and Fig. S2. It can be seen from Fig. 4a that the average sizes of the DHLA-Au NCs are ca. 1.8 nm. The lattice spacing is measured to be 0.235 nm, which is similar to previous paper about Au NCs.<sup>26,27</sup> No aggregation has been observed. As well as this, no significant difference has been found by the comparison of TEM for DHLA-Au NCs prepared in the absence and presence of 0.5 and 1.5 M of NaSC. On the other hand, some aggregates can be found in Fig. 4d. Based on the corresponding size distribution diagrams (Fig. S1d), both ultra-small size nanoclusters and big size (> 4nm) nanoparticles exist. This is in agreement with the broad fluorescence emission peak for DHLA-Au NCs prepared in the presence of 2.0 M NaSC. Additionally, it can be seen from Fig. 3b that the fluorescence intensity decreases. Thus, the aggregation will cause the quenching of the fluorescence rather than enhancement. As well as this, DLS study for average size and zeta potential was displayed in Fig. S2 and Fig. S3. The error bar for DHLA-Au NCs prepared in the presence of 2.0 M NaSC is relatively large, but the error bars for other studied DHLA-Au NCs are narrow, which further confirm that the Au NCs haven't aggregated until 2.0 M NaSC was used. Base on the zeta potential in Fig. S3, it is also concluded that the as prepared Au NCs are stable until 1.5 M NaSC has been used. Therefore, it indicates that the fluorescence can not only be enhanced in the presence of 0.5 and 1.5 M NaSC, but also the as prepared Au NCs are stable. In summary, it can be concluded that the fluorescence enhancement was not caused by aggregation.

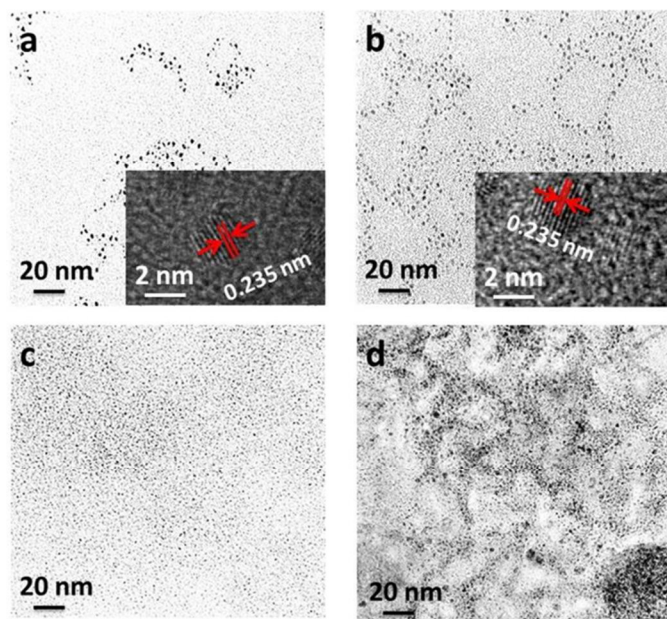


Fig. 4 TEM study for the as prepared DHLA-Au NCs in the absence (a) (inset describes the lattice fringes of Au), and presence of 0.5 M (b), 1.5 M (c) and 2.0 M (d) of NaSC salt.

XPS studies were used to characterize DHLA-Au NCs prepared in the presence of 0.5 M and 1.5 M of NaSC, see Fig.

S4. Fig. S4a describes the binding energy of Au 4f<sub>5/2</sub> and Au 4f<sub>7/2</sub> at 88.0 eV and 84.4 eV, respectively. Fig. S4b describes the binding energy of Au 4f<sub>5/2</sub> and Au 4f<sub>7/2</sub> is located at 88.0 eV and 84.3 eV, respectively. Their binding energies are quite similar. It can be seen that the binding energies of Au 4f<sub>7/2</sub> lie between Au(0) (84.0 eV) of a metallic gold and Au(I) (86.0 eV) of gold thiolate, which is similar to previously reported Au NCs, suggesting the coexistence of Au(0) and Au(I) for DHLA-Au NCs prepared in the presence of salt.<sup>28-30</sup> As well as this, it is noted that both Au 4f<sub>5/2</sub> and Au 4f<sub>7/2</sub> for the new DHLA-Au NCs in the presence of salt show blue shift compared to the original reported DHLA-Au NCs that locates at 88.3 and 84.6 eV.<sup>24</sup> This can be caused by the different charge transfer effect between DHLA and gold core due to the adsorption of more ligands. These characterizations reveal DHLA-Au NCs in the presence of salt (0.5 M, 1.5 M) describe similar properties to the previously reported DHLA-Au NCs.

Based on the above results, it can be seen that the fluorescence of DHLA-Au NCs is influenced by the concentration of NaSC salt. For NaSC solution, the ionic strength is proportional to the concentration according to the following equation, where *I* is the strength of the salt, *C* is the concentration, and *Z* is the charge.

$$I = \frac{1}{2} \sum_{i=1}^n C_i Z_i^2$$

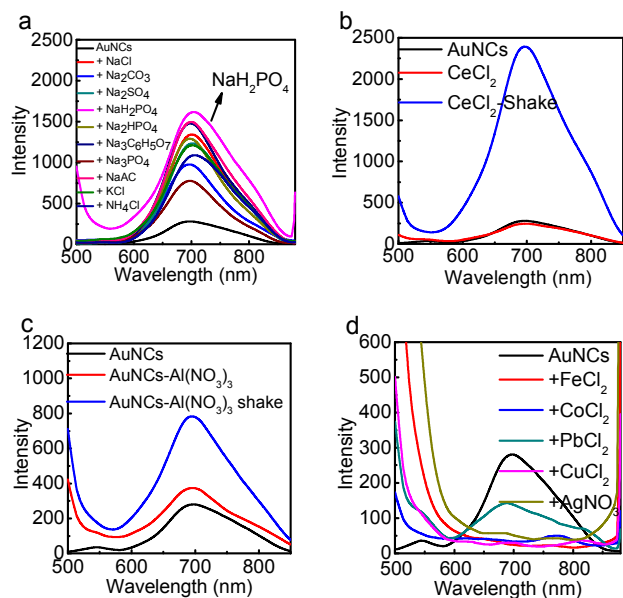
Thus, it can be concluded that the fluorescence intensity changes as a function of the strength of NaSC. It is worth investigating whether the fluorescence is just influenced by strength of salt. Afterwards, we performed a series of other metal salts to study the fluorescence change, see Fig. 5. Firstly, we investigated various sodium salts, KCl, and NH<sub>4</sub>Cl on the fluorescence behaviours of DHLA-Au NCs with the same strength, see Fig. 5a. It can be seen that all the studied salts describe assistance for the enhancement of the fluorescence of DHLA-Au NCs and their enhancement tendency is similar. However, in the presence of NaH<sub>2</sub>PO<sub>4</sub>, light scattering effect can be observed. This is not surprising because NaH<sub>2</sub>PO<sub>4</sub> affects the water solubility of DHLA-Au NCs as well as the acidity condition. Thus, the light scattering effect in the fluorescence spectrum was observed. Notwithstanding, the enhancement of fluorescence intensity was still observed. Additionally, it can be concluded that the anions barely influence the enhancement for the fluorescence since NaAC (Sodium acetate) and NaCl describe similar fluorescence enhancement though they are with different anions.

Additionally, the fluorescence intensity also was increased by the addition of rare earth metal salts such as CeCl<sub>3</sub>, see Fig. 5b. However, after 5 minutes, the fluorescence was gradually decreased to its original level. This was because the addition of CeCl<sub>2</sub> not only changed the surface condition of Au NCs, but also some precipitate was formed. According to the reported paper, OH<sup>-</sup> can stably bind to Au<sup>+</sup> on the cluster surface.<sup>31</sup> Herein, OH<sup>-</sup> was interacted with both Au<sup>+</sup>

and  $\text{Ce}^{3+}$  to form Au NCs-OH-Ce as well as  $\text{Ce}(\text{OH})_3$ . After the shake of the suspension, the fluorescence describes enhancement again. Similar to the salts in Fig. 5a,  $\text{CeCl}_3$  could lead to an enhancement for the fluorescence of DHLA-Au NCs. The insoluble products contain both  $\text{Ce}(\text{OH})_3$  and Au NCs-OH-Ce. After PBS buffer was used to disperse the precipitate, the fluorescence enhancement of DHLA-Au NCs could also be described.

As well as this, it is interesting to find that  $\text{Al}(\text{NO}_3)_3$  describes similar phenomena like the  $\text{CeCl}_3$  salts, see Fig. 5c, though the enhancement is not completely recovered after the shaking. This is possibly caused by the formation of more amounts of  $\text{Al}(\text{OH})_3$  precipitate. It reveals their enhancement mechanisms are probably similar. It also indicates that rare earth metal salt such as  $\text{CeCl}_3$  and amphoteric metal salt such as  $\text{Al}(\text{NO}_3)_3$  can be used for the enhancement of fluorescent Au NCs by carefully controlling the conditions.

Furthermore, heavy metal salts including  $\text{FeCl}_3$ ,  $\text{CoCl}_2$ ,  $\text{PbCl}_2$ ,  $\text{CuCl}_2$  and  $\text{AgNO}_3$  were studied, see Fig. 5d. The fluorescence was partly quenched in the presence of 0.1 M of  $\text{PbCl}_2$  and completely quenched by other studied metal salts. As is commonly known, the carboxyl ligand in DHLA could complex with these heavy metal ions at high concentrations. Then, the complex induced the quenching of fluorescence. After further shaking the mixture of these heavy metal salt and DHLA-Au NCs, no fluorescence could be observed anymore. The phenomena are different from DHLA-Au NCs in the presence of  $\text{Ce}^{3+}$  or  $\text{Al}^{3+}$  salts.



**Fig. 5** Fluorescence spectra of DHLA-Au NCs in the presence of soluble alkali salt (a), rare earth salt (b), amphoteric metal salt (c) and heavy metal salt (d). Note, since the water solubility of different salts are different, different concentrations of salts are used. The strengths of ions in part (a) are same as 1.5 M of NaSC; The strengths of part (b) and part (c) are same as 0.1 M of  $\text{CeCl}_3$ . The strengths of metal salts in part (d) are same as 0.1 M of  $\text{FeCl}_2$ .

Based on the above results, it can be seen that the fluorescence behaviour is not only influenced by the concentration of salts, but also affected by the species of salts. This work inspires the exploration of new routes for the fluorescence enhancement of noble metal nanoclusters.

## Conclusions

A simple approach to enhance the fluorescence of DHLA protected gold nanoclusters for almost 10 times by the assistance of Sodium citrate is proposed. Additionally, it is found  $\text{NH}_4^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  salts can be used for the enhancement of the fluorescence. However, light scattering as well as fluorescence enhancement is demonstrated in the presence of  $\text{NaH}_2\text{PO}_4$ .  $\text{CeCl}_3$  and  $\text{Al}(\text{NO}_3)_3$  salts describe light scattering effect as well as the fluorescence enhancement effect after shaking. Finally, it is found the fluorescence will be quenched in the presence of heavy metal salts.

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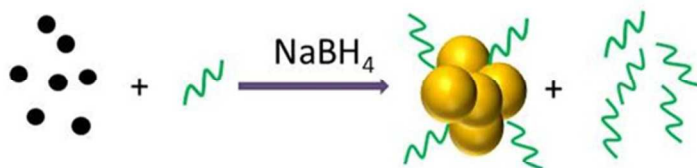
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## Fluorescence enhancement of DHLA protected gold nanoclusters in the presence of salt

Dan Li, Zhenhua Chen\*, Tiezhu Yang

The mechanism for the enhancement of DHLA protected gold nanoclusters has been investigated based on the adsorption of thiolate ligand.

a



b

