



## Hexamacrocycle assisted sensing of silver ion through facile synthesis of silver nanoparticles

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### ABSTRACT

The ease of generation of silver nanoparticles by using hexamacrocycle ligand, **L1** is utilized for the visual detection of the presence of silver ions at lower concentrations.

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Selective recognition of analytes, such as metal cations, anions, and biomolecules has huge impact on environmental monitoring and developmental biology.<sup>1</sup> Silver compounds are widely used in many industrial applications and silver gets accumulated in the environment, which may lead to toxicity on overexposure.<sup>2</sup> A few reports on the detection of Ag<sup>+</sup> ion are available which are either expensive or time consuming in nature.<sup>3–7</sup> Rhodamine-B,<sup>4</sup> coumarins,<sup>5</sup> calixarenes,<sup>6</sup> and crownethers<sup>7</sup> are some of the organic compounds employed for sensing silver ions. They interact with appropriate analyte whereupon the change in optical properties<sup>4–7</sup> like fluorescent enhancement/decrement or visual color change is observed.

Use of nanomaterials for sensing of analytes is a topic of current interest and is being explored actively.<sup>3,8</sup> In contrast, conversion of analytes (e.g., metal ion) to nanoparticles (metal nanoparticles) using explicit reaction parameters where a distinct visual change could be observed may comprise as a new approach of the detection of the analytes. Additionally, the method will be of practical importance provided the reaction conditions employed for such experiments are simple to perform and the detection is successful at lower concentration of the metal ion irrespective of the counter anion. Metal nanoparticles are known to exhibit characteristic surface plasmon absorption by the oscillation of conduction electrons.<sup>9</sup> Silver nanoparticles (AgNPs) exhibit surface plasmon absorption in the visible region which falls around 420 nm.<sup>9</sup> The solution containing AgNPs exhibit bright color whose hue and

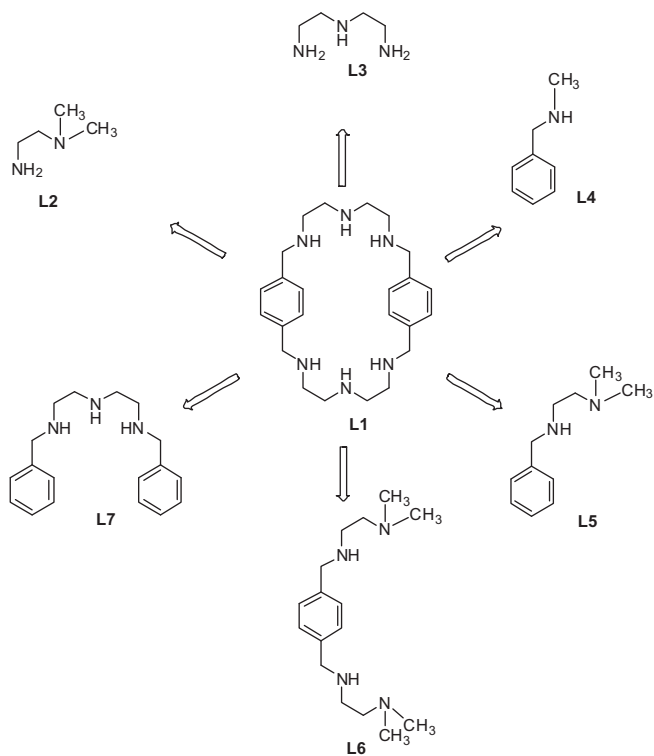
intensity depend on the setting provided by the reaction parameters.<sup>10</sup>

Silver ions can be reduced to Ag(0) by mild reducing agents and can be stabilized as nanoparticles in the presence of a stabilizer.<sup>11</sup> Synthesis of AgNPs is attractive when the stabilizer performs the dual function of reduction and stabilization. Some amine based stabilizers of AgNPs also act as reducing agents during the preparation of AgNPs where the electron transfer ability of the amines helps in the reduction step.<sup>12</sup> Herein, we report facile synthesis of AgNPs at room temperature by simply mixing an aqueous solution of silver acetate with a methanolic solution of the cyclophane type polyazamacrocycle, **L1** (Fig. 1). Immediate reduction of the metal ion giving stable AgNPs was observed even at lower concentration of various silver salts thus making the method practically valuable.

The macrocycle **L1** reported by Martell<sup>13</sup> can be prepared very easily by [2+2] condensation of terephthalaldehyde with diethylenetriamine followed by reduction using NaBH<sub>4</sub>. This ligand forms a variety of binuclear complexes which are utilized as efficient host/models in supramolecular and bioorganic chemistry.<sup>14–16</sup> We have demonstrated the dual role of the macrocycle **L1** for efficient synthesis of AgNPs as a novel method. The superstructure of the macrocycle is apparently responsible for the dual nature.

The synthesis of AgNPs is achieved by simply combining 2 mL of 2 mM aqueous solution AgOAc with 1 mL of 2 mM methanolic solution of the macrocycle. This combination leads to the development of a yellow colored solution. As the methanol solution of macrocycle interacts with Ag<sup>+</sup> ion immediate reduction occurs which could be ascertained by the appearance of a characteristic surface plasmon peak of the soluble Ag(0) species (Fig. S1, Supple-

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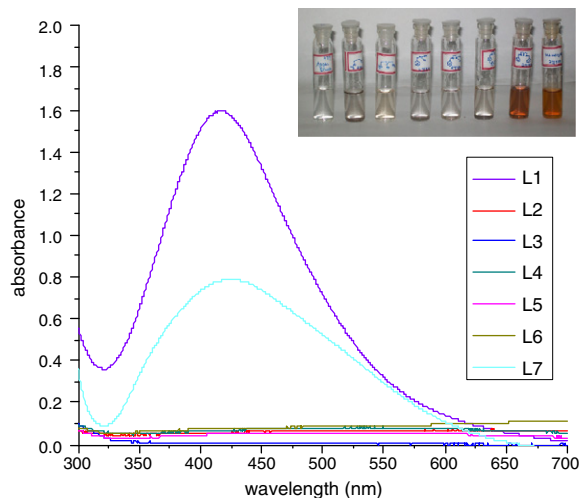


**Figure 1.** The amine ligands **L1–L7** used in the synthesis of AgNPs.

mentary data). The change in optical properties of the solution was monitored by recording a set of UV–vis spectra of the solution as a function of time. The material was further characterized by powder XRD, TEM, HRTEM, and EDAX (Figs. S2, S3 and S4, Supplementary data).

The unique role of **L1** was further substantiated by replacing the macrocycle with a few other amines (**L2** to **L7**) (Fig. 1) for the synthesis of AgNPs while keeping other conditions fixed. These amines could be considered as parts of the super-structure of **L1**. Here the UV–vis spectra and photograph of the samples were taken after standing the solutions for 12 h. The oxidation potential of the amines is found to be above 0.8 V (Fig. S5, Supplementary data), which is required for the reduction of silver ion. Thus, the ligands (**L1** to **L7**) assisted in the reduction of  $\text{Ag}^+$  ions as expected. Among the amines used, **L1** and **L7** showed reduction giving yellow colored solutions (Fig. 2). The solutions containing the other amines (i.e., **L2** to **L6**) did not show any color, however, deposition of black particles at the bottom of the container indicates reduction. It is worth mentioning here that the solubility behavior of AgNPs prepared in presence of **L1** and **L7** is not the same. Dark colored precipitate was formed with time in case of the AgNPs solution generated using **L7** where the precipitate is deposited at the wall and bottom of the glass container (Fig. S6, Supplementary data). In the case of the AgNPs solution prepared by using **L1**, no precipitate could be seen. Hence the superiority of the macrocycle over the acyclic counter parts for the facile synthesis and stabilization of the AgNPs is established.

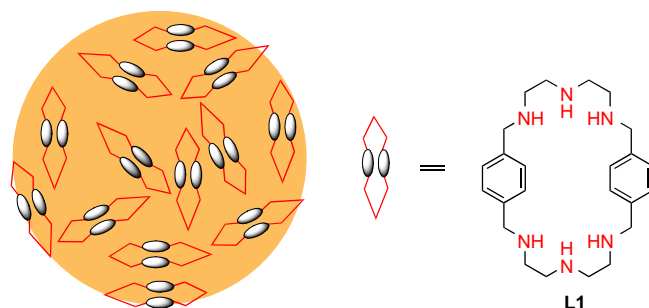
Various azamacrocyclic derivatives<sup>17</sup> are found suitable for encapsulation of  $\text{Ag}^+$  ion also established by convincing crystal structures. The color of the solutions may become dark with occasional precipitation during the complexation reactions when performed in systems containing methanol attributable to the reduction of silver ion. Therefore during the synthesis of AgNPs mentioned in this work we assume coordination of the metal ion at the beginning stage when the reduction is favored due to prox-



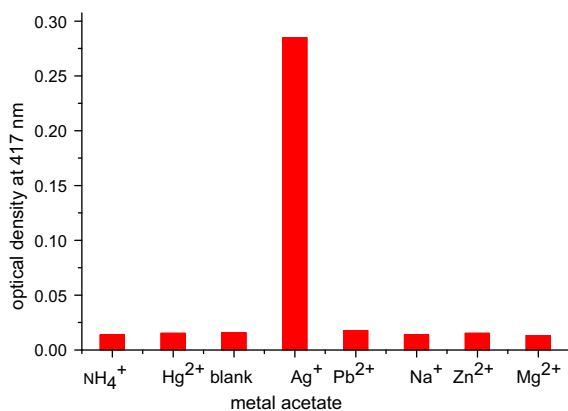
**Figure 2.** UV–vis absorption spectra of the samples obtained from the combination 2 mL of 2 mM aqueous solution AgOAc with 1 mL of 2 mM methanolic solution of the ligands **L1** to **L7** which were allowed to stand for 12 h. Photograph shows the appearance of the solutions which were allowed to stand for 12 h (from left to right, blank, **L2** to **L7**, and **L1**).

imity of the metal ion to the amine centers. Although ligand **L7** could stabilize the Ag(0) species formed as AgNPs for longer time as compared to **L2–L6** nevertheless some amount of precipitate was observed with time. However, the macrocycle **L1** shows no precipitation of the AgNPs that can be attributed to the cyclic nature of the ligand which not only helps in facile reduction but also found to be instrumental in the stabilization. Proton NMR spectrum of the ligand **L1** was recorded in a mixture of  $\text{D}_2\text{O}$  and  $\text{MeOH-}d_4$  followed by addition of 2 equiv. of AgOAc and further spectra were obtained after 30 min and 3 h (Fig. S7, Supplementary data). The peaks due to the methylene protons got broadened indicating interaction of the amine centers with the AgNPs formed. The proposed model of the **L1** stabilized AgNPs is shown (Fig. 3) schematically where the spherical type AgNPs are proposed to be covered by the macrocycle randomly. Other ligands (**L2** to **L6**) showed the reduction of silver ions and concomitant precipitation thereby the solution remained colorless. This indicates that **L1** provides maximum stability of the AgNPs over other ligands. For this reason the ligand **L1** was chosen for further study with respect to the detection of silver ion where the formation of stabilized nanoparticles is a prime requirement.

To a solution of macrocycle in methanol (4 mL of 2 mM) varied concentration of 0.1 mL of aqueous solution of silver acetate were added so as to assess the lower detection limit of silver ion. The concentration of the silver ion falls in the range of 14.6–365.8  $\mu\text{M}$



**Figure 3.** A representative picture showing the possible interaction of **L1** with AgNPs.



**Figure 4.** A comparison showing optical density (at 417 nm) of various solution obtained from the combination of 4 mL of 2 mM of methanolic **L1** with 0.1 mL of 1 mM of aqueous metal acetates after standing for 30 min.

in the final solutions. It is shown clearly that Ag<sup>+</sup> ion can be visually sensed at low concentrations (Fig. S8, Supplementary data). A linear correlation exists between the absorbance at 420 nm as increase in the concentration of Ag<sup>+</sup> ions over the range of 10<sup>-5</sup>–10<sup>-4</sup> M concentration with the relative coefficient of 0.996 is exhibited. (Fig. S9, Supplementary data). The formation of Ag nanoparticles was confirmed by the appearance of the surface plasmon peak in TEM image and UV–vis spectra (Figs. S10 and S11, Supplementary data).

The formation of AgNPs from other silver salts having a range of counter anions was performed at lower concentration of the silver ion (~24 μM). Silver salts such as AgBF<sub>4</sub>, AgPF<sub>6</sub>, AgCF<sub>3</sub>SO<sub>3</sub>, AgNO<sub>3</sub>, AgCl, and AgOAc were taken for this study. All the solutions behaved similarly and showed the formation of AgNPs which was monitored by UV–vis spectroscopy (Figs. S11 and S12, Supplementary data). This suggests that, anions have little/no interference in detection of silver ion under the condition employed.

When the experiments were performed using other metal acetates, such as NH<sub>4</sub><sup>+</sup>, Hg<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, Pb<sup>2+</sup>, and Zn<sup>2+</sup> and other metal chlorides, such as Ba<sup>2+</sup>, Ca<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>3+</sup>, Hg<sup>2+</sup>, K<sup>+</sup>, Li<sup>+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, and Zn<sup>2+</sup>, the solution remained colorless. The absorbance of a variety of metal acetates at 417 nm is shown (Fig. 4), which implies the selectivity of silver ions over other metal cations.

We tested the selectivity of silver ions in the presence of ten fold excess of other metal ions such as Na<sup>+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, Pb<sup>2+</sup>, and Zn<sup>2+</sup>. To the methanolic solution of **L1** (4 mL of 2 mM) was added 0.1 mL of aqueous solution of 1 mM of AgOAc and also 0.2 mL of aqueous solution of 5 mM of other metal acetates. As shown in (Fig. S13, Supplementary data) the presence of other metal ions did not lower the absorbance rather, result in the slight increase in absorbance in the presence of other metal ions. This is possibly due to the growth of the AgNPs size due to the presence of additional metal salts which can act as seed.<sup>18</sup>

In conclusion, we have reported a room temperature synthesis of AgNPs demonstrating the special role of a hexazamacrocyclic ligand in aqueous–methanol. The ligand helps in reduction and substantial stabilization probably through coordination and cation–π interaction attributed to the cyclic nature of the ligand. The ease of generation of silver nanoparticles is utilized for the visual detection of the presence of silver ions at lower concentrations. Exploration of such methodology can be useful for detecting other metal cations by infusing the concepts of supramolecular chemistry and nanochemistry.

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## Supplementary data

Supplementary data (synthesis of ligands, details of materials characterization and property evaluation by UV–vis, powder XRD, TEM, HRTEM, EDAX, CV and NMR methods and other graphs) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.10.091.

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