



CHEMISTRY & BIOLOGY INTERFACE

An official Journal of ISCB, Journal homepage; www.cbijournal.com

Sensing and quantification of Hg²⁺ ions based on aggregation of carbamatelinked-triazole stabilized silver nanoparticles

Kashmiri Lal^{1*}, Poonam Rani¹ and Rahul Shrivastava²

^aDepartment of Chemistry, Guru Jambheshwar University of Science and Technology, Hisar-125001, India ^bDepartment of Chemistry, Manipal University Jaipur, VPO-Dehmi Kalan, Of Jaipur-Ajmer Expressway, Jaipur, Rajasthan, India *Corresponding author. Tel.: +91 1662 263152; fax: +91 1662 276240

E-mail address: klal_iitd@yahoo.com (Kashmiri Lal)

Received 16 November 2018; Accepted 10 April 2019

Abstract: A (1-(4-bromobenzyl)-1H-1,2,3-triazole-4-yl)methyl(4-bromophenyl)carbamate and (1-(4-methylbenzyl)-1H-1,2,3-triazole-4-yl)methyl(4-bromophenyl)carbamates (**4a-4b**) have been successfully synthesized by reacting prop-2-yn-1-yl(4-bromophenyl)carbamate (**2**) with 4-bromo benzyl bromide (**3a**) and 4-methyl benzyl bromide (**3b**) using cellulose supported cuprous iodide nanoparticles and water as solvent. These synthesized triazoles were utilized for the stabilization of silver nanoparticles. The triazole stabilized silver nanoparticles were further examined for their ion sensing ability towards various cations like, Hg²⁺, Cd²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Cr²⁺, Co²⁺, Fe²⁺, Ni²⁺, Ca²⁺, Mg²⁺ and Mn²⁺ ions. The colorimetric and UV-visible studies revealed that stabilized AgNPs selectively sense Hg²⁺ ion in preferences to other cations. Transmission electron microscopy (TEM) images clearly indicated that addition of Hg²⁺ to a solution of stabilized AgNPs triggered the aggregation of silver nanoparticles due to which there occurs change in color from dark orange to colorless. The detection limits of AgNPs stabilized by **4a** and **4b** for Hg²⁺ ions was found to be 4.1×10⁻⁶ M and 3.67×10⁻⁷ M, respectively. The present paper provides an easy and selective colorimetric approach for detection of mercury ion.

Keywords: Carbamates, 1,2,3-triazoles, silver nanoparticles, chemosensors, Hg²⁺ sensors

Introduction

The design and development of simple and sensitive analytical methods for sensing of toxic metal ions have received significant consideration in recent times because of the

toxicological effects of these metals on human and animal health, plant metabolism and on soil biological activity.¹⁻³ Mercury is known as extremely toxic metal ion which causes adverse effects on human health, environment and ecological safety⁴⁻⁶ due to its highly reactive nature towards sulfthydryl group of enzymes and protein which enhances its bio-accumulative properties.⁷⁻⁸ Therefore, World health Organization and Environmental Protection Agency offers the maximum permissible limits of mercury ion in drinking water up to 5 ppb and 2 ppb, respectively.⁹⁻¹⁰ Considering the hazardous effects of mercury ion, the design and development of highly sensitive and selective analytical tool for detection of mercury ion at low level concentration are an exciting area of research.¹¹⁻¹²

There are various methods for the detection of mercury ions at low concentration including atomic absorption spectroscopy,¹³ cold vapour atomic fluorescence spectrometry,¹⁴ X-ray absorption spectroscopy¹⁵ and inductively coupled plasma mass spectroscopy.¹⁶ However, these methods require expensive sophisticated instruments, trained operator and are difficult for on-site assay. Further, several fluorescent, chromomeric, luminescent based molecules have also been reported for efficient sensing of mercury ions at low concentration.¹⁷⁻²⁰ Colorimetric detection of mercury and other toxic ions in aqueous solution is an efficient approach as it involves least instruments and fast response via ion induced color change of solution.²¹⁻²⁵ In this context, silver nanoparticlesbased sensors have drawn significant attention due to their high extinction coefficient, low toxicity, good stability and unique surface plasmon resonance absorption properties.²⁶⁻³¹

The copper(I)-catalyzed click reactions has received much attention because of its numerous applications in medicinal chemistry,³² material chemistry³³ and bioconjugation.³⁴ 1,4-Disubstituted 1,2,3-triazoles have also found numerous applications in supramolecular³⁵ and coordination chemistry³⁶ because of their excellent capabilities to exhibit variety of noncovalent interactions with host analytes.³⁷ 1,2,3-Triazoles are versatile ligands offering various binding sites for metal coordination

via either N2, N3 or C5 atoms.³⁸⁻⁴⁰ The role of 1.2.3-triazoles as a potential ligand with Hg²⁺ ion chelating ability has been highlighted in literature. For instance, Anjul et al. reported some bile acid derived triazoles with high selectivity and sensitivity towards Hg²⁺ ions.⁴¹ Arasappan and co-workers studied some sugartriazole based molecules with high affinity for Hg²⁺ ions.⁴² Keeping in view of the above, it was planned to synthesize some molecular architectures containing 1,2,3-triazole and carbamate moieties for stabilization of silver nanoparticles. Therefore, herein, we report the synthesis of carbamate-linked 1,2,3-triazoles and investigated their silver nanoparticles stabilizing ability and ion sensing properties. We found that carbamate-linked 1,2,3-triazole ligand stabilizes silver nanoparticles in presence of sun light and exhibited selective colorimetric sensing for the mercury ion via visual colour change from dark orange to colorless solution.

Results and Discussion

The synthesis of carbamate linked 1,2,3-triazoles (4a-4b) is depicted in scheme 1. In the first step the prop-2-yn-1-yl (4-bromophenyl)carbamate (2) was synthesized from 4-bromo phenyl isocyanate (1) and propargyl alcohol using N,N-dimethyl amino pyridine in dichloromethane. Prop-2-yn-1-yl (4-bromophenyl)carbamate was then subjected to one-pot multicomponent reaction with 4-methyl or 4-bromo benzyl bromides (3a-3b), sodium azide and catalytic amounts of cellulose supported cuprous iodide nanoparticles in water⁴³ vielding the 1,2,3-triazoles (4a-4b) in good to high vield at 80°C.



Scheme 1 Synthesis of carbamate-linked 1,4-disubstitutesd 1,2,3-triazoles (4a-4b): Reagents and conditions: (i) Propargyl alcohol, N,N-dimethyl amino pyridine, DCM. (ii) Substituted benzyl bromide, sodium azide, cuprous iodide nanoparticles catalyst, and water (10 mL), 80 °C.

The structures of both the carbamate-linked 1,2,3-triazoles (4a-4b) were confirmed on the basis of their FTIR, ¹H NMR, ¹³C NMR and HRMS spectral data. The FTIR spectrum of compound 4a, showed a characteristic N-H stretching band at 3401 cm⁻¹, whereas C=O stretching bands of ester and amide groups were observed at 1734 cm⁻¹ and 1593 cm⁻¹, respectively. The ¹H NMR spectra of compound 4a exhibited a characteristics singlet at δ 7.66 corresponding to triazolyl proton. The two sets of methylene protons were observed at δ 4.80 and δ 5.40. The ^{13}C NMR spectrum of compound 4a exhibited characteristic peaks at δ 143.44 and δ 120.31 due to C-4 and C-5 carbon atoms of the triazole ring. While, two methylene carbons resonated at δ 58.13 and δ 53.57 ppm. The mass spectrum of 4a showed a peak at m/z 466.9529 $(M+H)^+$ which is in good agreement with the molecular formula of the compound. These synthesized carbamatelinked 1,2,3-triazoles (4a-4b) were used for the synthesis of silver nanoparticles. The silver nanoparticles were synthesized by the reduction of silver nitrate by visible light in the presence of carbamate-linked 1,2,3-triazole as per literature procedure (scheme 2).⁴¹ The solution of silver nitrate (2 μ M) in a mixture of CHCl₂/ MeOH (7:3) was slowly added to the solution of the 4a (2 μ M) in CHCl₂/MeOH (7:3) and the resultant solution was exposed to sun light for 20-30 minutes. It was interesting to observe that colourless solution turned to dark orange within 15 minutes, which clearly indicated the formation of carbamate-linked 1,2,3-triazole stabilized silver nanoparticles. Further, to verify the role of 4a-4b in the formation of silver nanoparticles, a reaction was carried out without addition of **4a-4b**. It was observed that colour of solution was not changed even after continuing exposure to the sunlight for 8 hours. The formation of 1,2,3-triazole stabilized silver nanoparticles was confirmed by TEM and FT-IR data. Transmission electron microscopy (TEM) image have shown particle size of the nanoparticles ranged from 8 nm to 45 nm and average size was found to be 27 nm (**Fig. 1** and **Fig. S18**). The FT-IR spectrum also confirmed carbamate-linked 1,2,3-triazole stabilized silver nanoparticles (**Fig. S15** and **S16**).





Fig. 1 TEM images of (a) silver nanoparticles stabilized with ligand 4a (b) silver nanoparticles stabilized with ligand 4b



Scheme 2 Synthesis of silver nanoparticles

The sensing behavior of silver nanoparticles stabilized by 4a and 4b towards different metal ions such as Hg²⁺, Cd²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Cr^{3+} , Co^{2+} , Fe^{2+} , Ni^{2+} , Ca^{2+} , Mg^{2+} and Mn^{2+} was investigated using colorimetric and UVvisible spectroscopic methods. Colorimetric sensing properties of triazole stabilized silver nanoparticles towards different metal ions were examined for visual colorimetric examination by addition 0.1 mL of perchlorate salts of metal ions (25 µM) to 2.5 mL of carbamate-linked 1,2,3-triazole-stabilized silver nanoparticles solution (2 µM). The addition of mercury ion to a solution of AgNPs led to the color changes from dark orange to colorless. However, no color change in solution of 4a was observed upon addition of other metal ions such as Cd²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Cr³⁺, Co²⁺, Fe²⁺, Ni²⁺, Ca²⁺, Mg^{2+} and Mn^{2+} ions as shown in Fig. 2. The observed colorimetric behavior of 4a-AgNPs upon addition of Hg²⁺ ions can be explained by Hg²⁺ triggered aggregation of AgNPs. The observed aggregation behavior of AgNPs can be explained by the formation of Ag-Hg amalgam through the partial transfer of electron density from silver to Hg²⁺ ion. The addition of Hg²⁺ ions to the 4a stabilized silver nanoparticles removed the carbamate-linked 1,2,3-triazole which has been used as a capping agent for the stabilization of silver nanoparticles which leads to a thermodynamically favorable redox reaction between Hg²⁺ and silver nanoparticles there by the color of solution changes from dark orange to colorless.44-47 Further, the selectivity of carbamate-linked 1,2,3-triazole-stabilized silver

nanoparticles towards Hg²⁺ ion was explored by addition of mixture of all tested metal ions to a solution of stabilized AgNPs which exhibited similar color changes as observed with Hg²⁺ ion, showing that the sensing Hg²⁺ ion is not interfered in presence of other metal ions. The TEM data also confirmed the Hg²⁺ ion triggered aggregation of AgNPs as depicted in **Fig. 3**.



Fig. 2 A Photographic image of the solution of AgNPs stabilized with ligand 4a





Fig. 3 TEM image of AgNPs stabilized with (a) ligand **4a** and (b) ligand **4b** after addition of Hg²⁺ ion

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To explore more insight about the selectivity of 4a-AgNPs towards various metal ions sensing, the UV-visible experiments were perofrmed by the addition of various metal ions such as Hg²⁺, Cd²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Cr³⁺, Co²⁺, Fe²⁺, Ni²⁺, Ca²⁺, Mg²⁺ and Mn²⁺ions in form of their perchlorate salts. In UV-visible spectrum of carbamate-linked 1,2,3-triazole-stabilized silver nanoparticles (4a-AgNPs) exhibited absorption peak at 248 nm and 511 mm as shown in Fig. 4. The absorption peak in UV region at 248 nm was assigned for carbamate linked 1,2,3-trizole moiety (4a) whereas peak in visible region at 511 nm was assigned for silver-nanoparticles. It was observed that upon addition of 25 µM solution of Hg²⁺ ions to a 2.0 µM solution of AgNPs stabilized by 4a, the intensity of absorption maxima at 248 nm was significantly increased whereas the peak at 511 nm was disappeared as shown in Fig. 4. On the other hand, other metal ions like Cd²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Cr³⁺, Co²⁺, Fe²⁺, Ni²⁺, Ca²⁺, Mg²⁺ and Mn²⁺ ions fail to exhibit any noticeable change in absorption spectrum. The observed spectral behavior can explained by the Hg²⁺induced aggregation of AgNPs. The AgNPs are oxidized by Hg²⁺, resulting in the formation soluble Ag(I). Afterward, the elemental Hg interacts with the surface of AgNPs, yielding the amalgam particles thereby removing the 4a from their surface as shown in scheme 3. The recovered carbamate-linked 1,2,3-triazole (4a) in the solution showed an intense peak at 248 nm in UV-visible spectrum.



Scheme 3: Detection of Hg²⁺ ions using 4a-AgNPs



Fig. 4: UV-visible spectra for the AgNPs stabilized with ligand **4a** solution (2 μ M, optical path length = 1 cm) after the addition of different equivalent of various metal ions



Fig. 5 UV-visible spectra for the triazole-**4a**-AgNPs (1.26×10^{-4} M) solution after the addition of different concentrations of Hg²⁺ (2.1×10^{-4} M to 5.7×10^{-3} M) over the interval of 5 minutes.

Furthermore, for the determination of detection limit of carbamate-linked 1,2,3-triazole stabilized silver nanoparticles for Hg²⁺ ion, the UV-visible absorption spectrum of blank test were measured. The standard deviation (α) of absorbance intensity for **4a**-AgNPs and **4b**-AgNPs at 248 nm were found to be 5.51×10⁻⁴ for **4a**-AgNPs and 1.1×10⁻⁴ for **4b**-AgNPs, respectively. The linear fitting were performed according to titration curves and slope was determined (**Fig. 6, Fig. 7, Fig. S20 and S21**; see supporting information). The limits of detection (LOD) of AgNPs stabilized by **4a** and **4b** were determined from the equation LOD = $3\alpha/S$, where, α is the standard deviation of the absorbance intensity of carbamate-linked 1,2,3-triazole stabilized silver nanoparticles of blank measurements, S is the slope of linear equation.⁴⁸⁻⁴⁹ The detection limits of the UV-visible spectrum for Hg²⁺ ion by **4a**-AgNPs and **4b**-AgNPs were found to 4.1×10^{-6} M and 3.67×10^{-7} M, respectively.



Fig. 6 Determination of detection limit for Hg^{2+} ion for **4a**-AgNPs. Absorbance Vs. Hg^{2+} concentration plot in **4a**-AgNPs. The standard deviation (α) of blank (**4a**-AgNPs) measurements = $5.51x10^{-4}$ (at 248 nm)



Fig. 7 Determination of detection limit for Hg^{2+} ion for **4a**-AgNPs from radiometric methods. Absorbance (248 nm/239 nm) Vs. Hg^{2+} concentration plot in **4a**-AgNPs. The standard deviation (α) of blank (**4a**-AgNPs) measurements = 5.51 x10⁻⁴ (at 248 nm)

These data clearly indicated that synthesized **4a** and **4b** stabilized AgNPs can detect mercury ion at low level concentration which is better or comparable with earlier reported methods.⁵⁰⁻⁵³

Experimental

Instrumentation, Analysis and Starting Material

Isocyanates, propargyl alcohol, benzyl halides, microcrystalline DMAP. cuprous iodide. cellulose were procured from sigma Aldrich and used as received. All the melting points (°C) were recorded in an open capillary using LABCO melting point apparatus. IR spectra were recorded on SHIMAZDU IR AFFINITY-I FT-IR spectrophotometer. The ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded using BrukerAvance-III 400 nano bay spectrometer. The high-resolution mass spectra (HRMS) were recorded using Micromass QTOF micro-mass spectrometer. HR-TEM images were obtained from JEOL JEM-3000F highresolution transmission electron microscope. The thin-layer chromatography (TLC) was performed on readymade silica gel plates and visualized under ultraviolet lamp.

Procedure for the synthesis of carbamatelinked terminal alkyne

To a stirred solution of propargyl alcohol (1.1 mmol) and DMAP (1.1 mmol) 30 mL of dichloromethane, phenyl isocyanate (1 mmol; dissolved in dichloromethane) was added drop wise at 0 °C. The stirring of reaction mixture was continued till the completion of reaction as monitored by TLC. After completion of the reaction, the reaction mixture was diluted with dichloromethane and the organic layer was washed with 2N sulphuric acid (2 × 10 mL), water (2 × 10 mL) and brine (10 mL) and dried over anhydrous sodium sulphate. Dichloromethane was evaporated in vacuum to

obtain the product.

Prop-2-yn-1-yl (4-bromophenyl)carbamate (2): off white solid, 91% yield, Mp: 124-126°C. IR (KBr, v_{max}/cm⁻¹): 3298 (NH str.), 2137 (C=C str), 1703 (C=O str, ester), 1638 (C=O str, amide), 1595, 1545, 1487, 1452, 1396, 1312, 1242 (C-O str, ester), 1111, 1070 (C-O str, ester), 1007, 980, 829, 764, 691, 646, 509. ¹H NMR (CDCl₂, 400 MHz): δ 2.55 (s, 1H, alkyne CH), 4.80 (s, 2H, CH₂), 6.72 (bs, 1H, NH), 7.28-7.32 (m, 2H, H3, H5), 7.43-7.46 (m, 2H, H2, H6). ¹³C NMR (CDCl₂, 100 MHz): δ 52.91 (OCH₂), 75.19 (CH-acetylene), 77.61 (C-acetylene), 116.45(2C, C4, C5), 120.31 (C1), 132.07 (2C, C2, C3), 136.50 (C6), 152.24 (C=O). HRMS: m/z (M+H)⁺ Cacld. for C₁₀H₈BrNO₂ 253.9817, found: 253.9804.

General Procedure for the synthesis of (1-(4-substitutedbenzyl)-1H-1,2,3-triazole-4-yl)methyl(4-bromophenyl)carbamates (4a-4b)⁴³:

A mixture of benzyl halide (1mmol), alkyne 2 (1mmol), sodium azide (1.2 mmol) and the catalyst (100 mg) in 10 mL of water was stirred at 80°C until TLC analysis shows that the reaction is complete. The reaction mixture was cooled to room temperature, filtered and residues thus obtained were washed with ethyl acetate. Solvent was evaporated under high vacuum to get corresponding 1,4-disubstituted 1,2,3-triazoles **4a-4b** in 71-88% yield.

(1-(4-bromobenzyl)-1H-1,2,3-triazole-4-yl) methyl(4-bromophenyl)carbamate (4a): Off white solid, 71% yield, Mp: 128-130°C. IR (KBr, v_{max} /cm⁻¹): 3401 (NH str.), 3136 (C-H str, triazole), 1734 (C=O str, ester),1701, 1643 (C=O str, amide), 1593, 1528, 1489, 1456, 1398, 1308, 1211 (C-O str, ester), 1057 (C-O str, ester), 1013, 820, 783, 567, 498. ¹H NMR (CDCl₃, 400 MHz): δ 4.80 (s, 2H, OCH₂), 5.40 (s, 2H, N-CH₂), 7.04 (bs, 1H, NH), 7.31-7.33 (m, 2H, Ar-H, 4``H and 5``H), 7.43-7.45 (m, 2H, 2`H,

3'H), 7.66-7.67 (m, 3H, 4'H, 5'H, triazolyl-H), 8.14 (s, 2H, 2''H, 3''H). ¹³C NMR (CDCl₃, 100 MHz): δ 53.57 (NCH₂), 58.13 (OCH₂), 116.23 (1''C), 120.31 (C-5), 123.11 (4'C, 5'C), 123.86 (1'C), 129.74 (4''C, 5''C), 132.03 (2''C, 3''C), 132.37 (2'C, 3'C), 133.32 (6''C), 136.71 (6'C), 143.44 (C-4), 153.02 (C=O). HRMS: m/z (M+H)⁺ Cacld. for C₁₇H₁₄Br₂N₄O₂ 467.1346, found: 466.9529

(1-(4-methylbenzyl)-1H-1,2,3-triazole-4-yl) methyl(4-bromophenyl)carbamate (4b): Off white solid, 88% yield, Mp: 139-141°C. IR (KBr, v_{max}/cm⁻¹): 3248 (NH str.), 3109 (C-H str, triazole), 1719 (C=O str, ester), 1667, 1591 (C=O str, amide), 1535, 1485, 1452, 1393, 1302, 1231 (C-O str, ester), 1119, 1072 (C-O str, ester), 1015, 814, 762, 691, 509. ¹H NMR (CDCl₂, 400 MHz): δ 2.37 (s, 3H, CH₂), 5.27 (s, 2H, OCH₂), 5.49 (s, 2H, N-CH₂), 7.20 (s, 4H, 2``H, 3``H, 4``H, 5``H) 7.28-7.32 (m, 3H, 2`H, 3'H, NH), 7.41-7.45 (d, 2H, 4'H, 5'H), 7.59 (s, H, triazolyl-H). ¹³C NMR (CDCl₂, 100 MHz): δ 21.15 (CH₂), 54.11 (NCH₂), 58.10 (OCH₂), 116.10 (4°C, 5°C), 120.33 (1°C), 123.75 (C-5), 128.23 (4``C, 5``C), 129.84 (2``C, 3``C), 131.25 (2°C, 3°C), 131.99 (6 °°C), 136.89 (1°°C), 138.89 (6°C), 143.16 (C-4), 153.10 (C=O). HRMS: m/z (M+H)⁺ Cacld. for $C_{18}H_{17}BrN_4O_2$: 401.0613, found: 401.0597.

Synthesis of triazole stabilized silver nanoparticles⁴¹:

For the synthesis of silver nanoparticles, 20 mL (2 μ M) solution of silver nitrate in chloroform/ methanol (7:3) was mixed with 20 mL (2 μ M) solution of the triazole in chloroform/methanol (7:3) and the mixture was exposed to sun light. The color of the solution becomes dark orange within 15 minutes indicating the formation of triazole stabilized silver nanoparticles.

Conclusion

In summary, we have reported the synthesis

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of carbamate-linked 1,4-disubstituted 1.2.3-triazoles (4a-4b)using cellulose supported cuprous iodide nanoparticles as a heterogeneous catalyst in good to excellent vield from carbamate-linked terminal alkvne via azide-alkyne cycloaddition reaction using water as solvent. These synthesized carbamate-1.4-disubstituted linked 1.2.3-triazoles (4a-4b) have been used for stabilization of silver nanoparticles. These carbamate-linked 1,4-disubstituted 1,2,3-triazoles stabilized silver nanoparticles showed remarkable colorimetric sensitivity and selectivity for mercury ion with detection limit of 4.1×10^{-6} M for triazole-4a-AgNPs and 3.67×10^{-7} M for triazole-4b-AgNPs. The present study may have an impact on the development of novel and selective chemosensors for the detection of mercury.

Acknowledgement

Authors are thankful to Central instrumentation laboratory, Guru Jambheshwar University of Science & Technology, Hisar and Manipal University Jaipur, Jaipur Rajasthan for running NMR and UV-Visible spectrum. Poonam Rani thanks University Grants Commission (UGC), New Delhi, India for the award of Junior Research Fellowship, respectively. Rahul Shrivastava acknowledge DST, Government of Rajasthan, India (P.7(3)S.T./R & D/2016/4871) for financial assistance.

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