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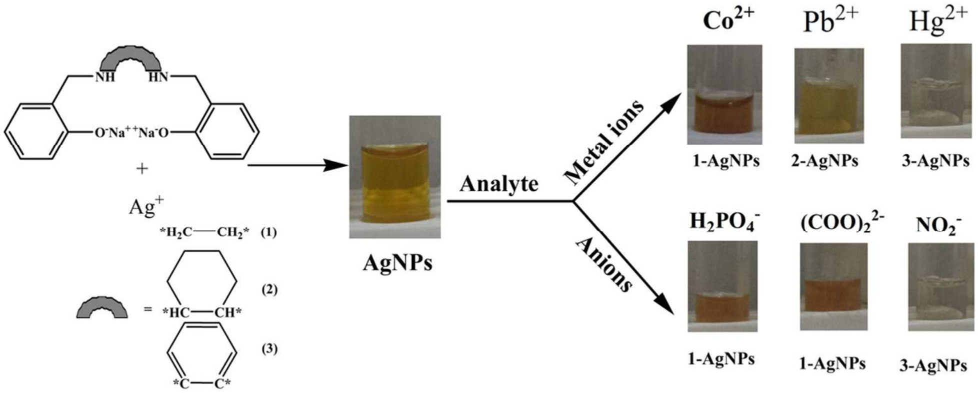

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ARTICLE TYPE

Coordinating ligand functionalized AgNPs for colorimetric sensing: Effect of subtle structural and conformational change of ligand on the selectivity

V. Vinod Kumar and Savarimuthu Philip Anthony*

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Metal coordinating C_2-symmetric phenolic chelating ligands (1-3) were used to prepare surface functionalized AgNPs for selective colorimetric sensing of metal cations and anions. The effect of subtle structural and conformational change of 1-3 on the colorimetric sensing was also explored. UV-Visible, IR spectroscopy and HR-TEM techniques were used to characterize AgNPs. Interestingly 1-, 2- and 3-AgNPs showed different colorimetric sensing of metal cations and anions. Aliphatic flexible diamine based 1-AgNPs showed selective sensing of Co^{2+} ions (10^{-7} M), oxalate and dihydrogen phosphate anions (10^{-6} M). Co^{2+} addition to 1-AgNPs produced brownish-orange colour whereas oxalate and phosphate resulted in brownish-pink colour due to aggregation. Alicyclic diamine based 2-AgNPs exhibited selective precipitate formation for Pb^{2+} ions without showing any anion sensing. The rigid diamine based 3-AgNPs showed selective decolourisation of yellow colour for Hg^{2+} and nitrite anions due to amalgamation and oxidation. Thus phenolic chelating ligands that have been used to generate versatile coordination networks with metal ions offered simple way to develop AgNPs based potential colorimetric sensor environmental screening.

Introduction

In recent years, there is a strong interest to design and develop simple, reliable, rapid and inexpensive sensor techniques for selective sensing of heavy metal ions and anions in water to asses the toxicity as well as to understand the biological role.[1–7] Hence different methods have been developed for the detection cations and anions, including atomic absorption spectroscopy, ICP-MS, electrochemical approaches and fluorescent analysis.[8-11] Although several fluorescent probes with high selectivity and sensitivity were reported,[4-7,11] colorimetric sensors have received significant attention in recent years because of their advantages such as naked eye detectable, cost effectiveness, simple and portable configuration that makes colorimetric approach as an on-site method for real time monitoring of analytes.[12-13] The recent advances in the field of nanoscience and nanotechnology have opened up new arenas for the applications of nanoscale materials including the development of ultrasensitive sensing and imaging methods in the analytical sciences.[14-18] Particularly, noble silver (Ag) and gold nanoparticles (AuNPs) draws greater attention for fabricating colorimetric assays due to their strong and unique localized surface plasmon resonance (SPR).[19-21] The strong and well defined colour of Ag and AuNPs due to excellent SPR properties makes easy for visualization of colour change.[22,23] The interparticles distance dependent SPR properties Ag or AuNPs provides practical platform for developing colorimetric sensors for various chemicals including toxic heavy metal ions and bio-molecules in aqueous solution. The surface modification of AgNPs with appropriate analyte interacting functionality is the key step in fabricating AgNPs colorimetric sensor.[24] For example, AgNPs with glutathione functionalization lead to selective sensing of Ni^{2+},[25] whereas pyridyl-appended calix[4]arene and dopamine functionalized AgNPs exhibited Fe^{3+} and Cu^{2+} colorimetric sensing, respectively.[26,27] Triazole functionalized AuNPs exhibited selective colorimetric sensing of Cr^{3+} ions whereas aptamer functionalization lead to selective sensing of K^+.[28,29] Mercaptothiadiazole fluorophore capped AuNPs showed selective sensing of Hg^{2+} and selective Co^{2+} sensing was reported with AuNPs modified with thioglycolic acid.[30,31]

Cobalt is an essential element for nutrition and its deficiency may cause anaemia, retarded growth and loss of appetite.[32] But consumption of large doses of cobalt may cause lung effects, which include respiratory irritation, asthma and pneumonia.[33] Mercury is one of the most toxic elements in the environment and poses serious health threats because of its high affinity for thiol groups in proteins and enzymes, thereby leading to the dysfunction of cells and consequently causing many health problems in the brain, kidney, and central nervous system.[34] Similarly lead, a second most toxic substance in the environment due to its wide distribution and uses,[35] can lead to neurological, reproductive, cardiovascular and developmental disorders even at low level exposure.[36] Children with variants in iron metabolism genes may be more susceptible to lead absorption and accumulation. Whereas phosphate anion is the important constituent of living systems and plays significant role in signal transduction and energy storage in biological systems.[37] However, excess of phosphate leads to algae and bacteria blooms, which is well-known as eutrophication.[38]

Similarly, carboxylate functionality is part of a wide range of biologically active entities, and in many cases is responsible for their biochemical properties.[39-42] For instance, the specific recognition and transport of dicarboxylates across biological membranes is crucial in the metabolism of cells,[39] and the mechanism of action of the vancomycin antibiotics is highly dependant on carboxylate binding.[40]

Subtle structural change of ligand is one of the simplest strategies that have been extensively employed in coordination chemistry to control or modify the mode of ligand coordination and resultant coordination network structure.[43-46] Phenol based chelating C_2-symmetric ligands have been widely used to generate coordination polymers and complexes with diverse topologies including helical structure.[47,48] The easy ionization properties of phenolic groups could be used to synthesis stable surface functionalized AgNPs.[49] This guest interacting surface functionality coupled with interparticle dependent AgNPs optical properties offered an opportunity to fabricate colorimetric sensor. In our lab, we have been working on the Ag and AuNPs based colorimetric assay for heavy toxic metal ions, anions and biomolecules. Green synthesized bio-functionalized AgNPs and amino acid attached phenolic ligands functionalized AgNPs for selective colorimetric sensing of Hg^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+} was reported recently.[50-52] Kyong et al studied the AgNPs shape dependent colorimetric sensing of metal ions.[53] Subtle structural change and conformationality of the ligand played important role to tune and control the topology of metal-organic framework in coordination chemistry. However, the effect of such subtle structural change of AgNPs surface functionality on the colorimetric sensing has been rarely investigated.

Herein, we report the synthesis of AgNPs with metal ion interacting surface functionality using three conformationally different C_2-symmetric phenolic chelating ligand and colorimetric sensing of metal cations and anions in aqueous solution. UV-Visible, IR and HR-TEM studies confirmed the formation of polydispersed AgNPs with phenolic ligands surface functionality. Interestingly, all three samples showed different metal cations and anions sensing (1-AgNPs for Co^{2+}, phosphate and oxalate, 2-AgNPs for Pb^{2+} (no anions) and 3-AgNPs-Hg^{2+} and nitrite). Co^{2+} (10^{-7} M) addition to 1-AgNPs produced brownish orange colour whereas phosphate and oxalate with 1-AgNPs showed brownish-pink colour. 2-AgNPs with Pb^{2+} exhibited selective precipitate formation. The rigid diamine based 3-AgNPs showed selective decolourisation of yellow colour for Hg^{2+} and nitrite ions. The controlled experiments suggest that Co^{2+} formed strong strong coordination with 1 and Pb^{2+} exhibited turbidity with 2 whereas 3 did not show any significant change with metal cations. Thus potential colorimetric sensor for heavy metal ions and anions with tunable selectivity has been developed using conformationally different phenolic chelating ligand.

Experimental Section

Salicylaldehyde, cyclohexane diamine, $NaBH_4$ and $AgNO_3$ were obtained from Sigma-Aldrich. Ethylene diamine, 1,2-diaminobenzene, ethanol and NaOH were obtained from Ranbaxy fine chemicals. Ortho phenylenediamine was re-crystallized from hot water in presence activated charcoal. The metal cations solution (10^{-3} M) used for the experiments were prepared by dissolving in Milli-Q water.

2.1. Synthesis of 1 (N, N'-bis(2-hydroxybenzyl)-1,2-diaminoethane), 2 (N, N'-bis(2-hydroxybenzyl)-1,2-diaminocyclohexane) and 3 (N, N'-bis(2-hydroxybenzyl)-1,2-diaminobenzene).

Reduced Schiff base phenolic chelating ligands, 1-3, was synthesized by following the reported procedure.[52] Typically 1 equivalent of diamine was dissolved 20 ml hot water and mixed with ethanol solution of salicylaldehyde (1 equivalent, 10 ml). The solution turned immediately bright yellow colour and the solution was heated at 80 °C for 30 min. The reaction mixture was cooled in ice-bath and $NaBH_4$ (1.5 equivalent) was added portion-wise. The bright yellow colour was slowly disappeared and neutralization of the reaction mixture produced precipitates of 1-3. The precipitate was filtered, washed with cold ethanol and dried in vacuum.

1. Yield = 85 %. ^1H NMR ($CDCl_3$) δ 7.12-7.23 (m, 4H), 6.76-6.84 (m, 4H, hydroxyl benzene), 4.18 (s, 4H), 3.48 (s, 2H), 3.21 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 156.1, 134.2, 132.3, 128.6, 125.2, 119.6, 48.2, 43.3. $C_{16}H_{20}N_2O_2$ (272.34): calcd. C 70.56, H 7.40, N 10.29; found C 70.80, H 7.31, N 10.20. m/z (LC-MS) 273.00 (M+H).

2. Yield = 83 %. ^1H NMR ($CDCl_3$) δ 7.17-7.24 (m, 4H), 6.79-6.87 (m, 4H), 4.11 (s, 4H), 3.42 (s, 2H), 3.18 (s, 2H), 1.78-1.89 (m, 4H), 1.45-1.61 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 155.8, 134.1, 132.5, 129.1, 124.3, 118.8, 59.4, 47.7, 32.4, 26.1. $C_{20}H_{26}N_2O_2$ (326.43): calcd. C 73.59, H 8.03, N 8.58; found C 73.64, H 8.35, N 8.30. m/z (LC-MS) 327.20 (M+H).

3. Yield = 80 %. ^1H NMR ($CDCl_3$) δ 6.85-6.94 (m, 4H), 6.56-6.71 (m, 4H), 6.30 (d, 2H), 6.22 (d, 2H), 4.38 (s, 4H), 3.88 (s, 2H). ^{13}C NMR ($CDCl_3$) δ 155.2, 133.3, 130.1, 129.4, 122.1, 116.7, 112.3, 33.6. $C_{20}H_{20}N_2O_2$ (320.38): calcd. C 74.98, H 6.29, N 8.74; found C 74.85, H 6.45, N 8.56. m/z (LC-MS) 321.00 (M+H).

2.2. Synthesis of 1-, 2- and 3-AgNPs

Silver nitrate (5 ml of 10^{-3} M) was added into aqueous solution of 1-3 (5 ml, 10^{-3} M) under stirring at 70 °C. 1-3 was dissolved in water using 1:2 molar ratio of NaOH. The immediate appearance of yellow colour suggested the reduction of silver ion into AgNPs. The solution was allowed to stir at that temperature for another 10 min. The reactions were repeated at least three times to confirm the reproducibility of AgNPs formation. The characterization of the synthesized AgNPs was carried out after allowing the solution to stand at room temperature for one day.

2.3. Characterization

The UV-visible measurement of the synthesized AgNPs were analyzed in a Perkin Elmer model UV–Vis double beam spectrophotometer from 250 to 800 nm, at the resolution of 1 nm. The powdered sample of 1-AgNPs was subjected to FT-IR spectroscopy measurement. These measurements were carried out on a Perkin–Elmer Spectrum-One instrument in the diffuse reflectance mode at a resolution of 4 cm^{-1} in KBr pellets.

The size and morphology of AgNPs were investigated using high resolution transmission electron microscopy (HR-TEM). Samples for TEM measurements were prepared by placing a drop of NPs solution on the graphite grid and drying it in vacuum. Transmission electron micrographs were taken using JEOL JEM-2100F operated at an accelerated voltage of 200 kV and an ultra high-resolution pole piece.

Result and Discussion

3.1. Synthesis and characterization

The phenolic chelating ligands 1-3 was synthesized by Schiff base condensation of diamine precursor with salicylaldehyde followed by $NaBH_4$ reduction in water-ethanol mixture. Addition of silver nitrate (10^{-3} M, 2 ml) into aqueous solution of 1-3 (10^{-3} M, 10 ml) at 70 °C produced brownish yellow coloured AgNPs solution. The intense colour of AgNPs is due to the strong surface plasmon resonance (SPR) vibration.[55] The phenolic compounds are known to reduce the silver ions and stabilize the AgNPs via electrostatic interactions of phenolic oxygen atoms (Fig. 1a).[49,56] The formation of clear and transparent brownish yellow colour confirmed the good dispersion of AgNPs. It is noted that aqueous solution of ligands alone did not show any colour (Fig. S2). The absorption studies of 1, 2 and 3-AgNPs exhibited typical AgNPs SPR absorption in the range of 380 to 435 nm (Fig. 1b). 1-AgNPs showed absorption λ_{max} at 380 nm whereas 2-AgNPs exhibited absorption at 415 nm. 3-AgNPs showed absorption λ_{max} at 435 nm. The size, morphology and crystallinity of the samples were analyzed using HR-TEM that showed the formation of spherical crystalline polydispersed AgNPs with size range of 10 nm to 30 nm (Fig. 2). FT-IR studies of 1-3 showed peak at 3453 - 3458 (N-H-stretch), 2900 - 2944 (C-H-stretch), 1591 – 1611 (C-H-stretch) and 1459 - 1479 (C-H-stretch) cm^{-1} and similar peak position with AgNPs confirms the surface coverage of phenolic chelating ligand (Fig. S3). It is noted that the inclusion of AgNPs with 1-3 lead to small shift in the peak position.

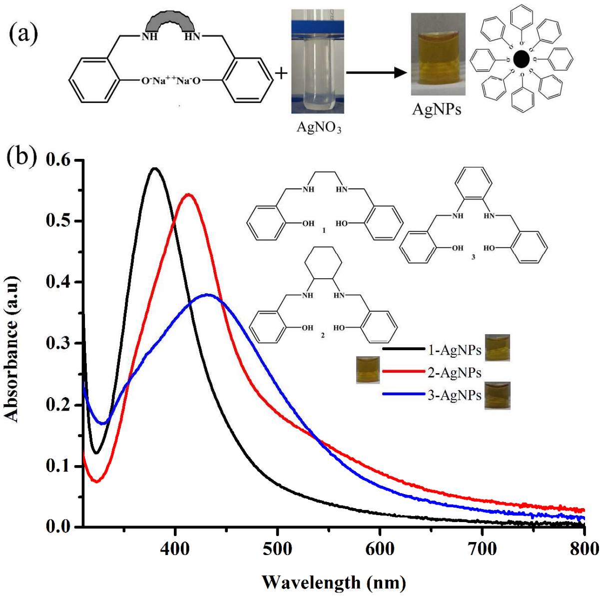


Fig. 1. (a) Schematic diagram of AgNPs synthesis using 1-3 and stabilization and (b) absorption spectra of AgNPs synthesized using 1-3. The molecular strucutre of 1-3 and digital images of 1-, 2- and 3-AgNPs are shown in the inset.

3.2. Colorimetric sensor studies of metal cations

The colorimetric sensing properties of 1-, 2- and 3-AgNPs were investigated by adding different metal ions into the AgNPs solution and monitoring the absorption as well as visual colour change. Interestingly, addition of Co^{2+} to 1-AgNPs resulted in the formation of brownish orange colour selectively (Fig. 3). Addition of other metal ions did not show any significant change in the 1-AgNPs colour. Absorption spectra of 1-AgNPs with different metal ions are shown in Fig. 3. 1-AgNPs showed absorption at 380 nm. The addition of Co^{2+} into 1-AgNPs produced new absorption at longer wavelength (527 nm) selectively. 1-AgNPs with other metal cations did not exhibit any significant change in the absorption spectra. The appearance of longer wavelength absorption was responsible for brownish-orange colour. The concentration dependent studies of 1-AgNPs clearly showed the appearance of longer wavelength absorption with increasing Co^{2+} (10^{-7} M) concentration (Fig 4a). The formation of new absorption peak at 527 nm was completed with the addition of 300 μL of Co^{2+} (10^{-7} M). The interference studies of 1-AgNPs for Co^{2+} (10^{-6} M) in presence of various metal cations (10^{-3} M) indicate the high selectivity. Co^{2+} addition to 1-AgNPs in presence of other metal ions also showed longer wavelength absorption (Fig. 4b) and suggest that other metal did not have significant influence on the Co^{2+} colorimetric sensing.

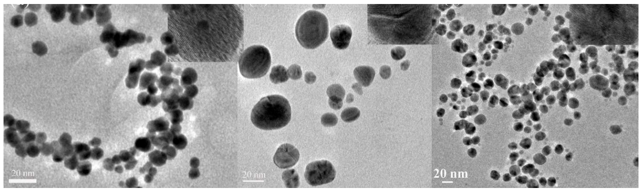


Fig. 2. TEM images of (a) 1-, (b) 2- and (c) 3-AgNPs. The inset of the figures shows the high resolution image of AgNPs.

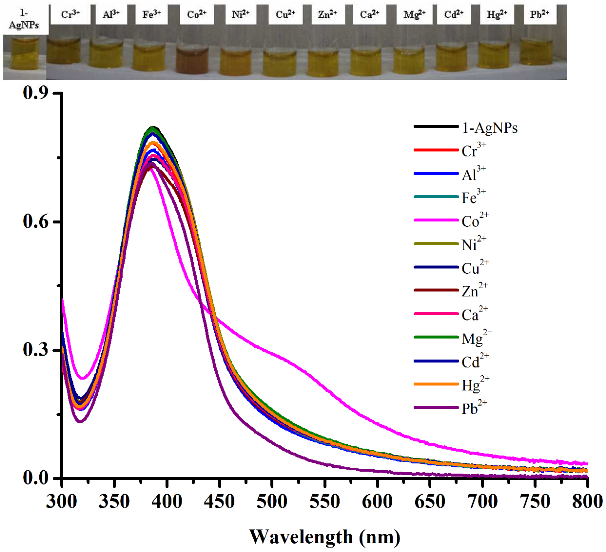


Fig. 3. Absorption spectra and digital images of 1-AgNPs with different metal cations (10^{-3} M).

In contrast, 2-AgNPs exhibited selective colorimetric changes for Pb^{2+} ions. 2-AgNPs with Pb^{2+} lead to the formation of precipitates (Fig. 5). Other metal ions including Co^{2+} addition did not show significant colour change or precipitate formation. Absorption spectra showed that Pb^{2+} addition into 2-AgNPs leads to slight decrease of absorption intensity at 415 nm but enhanced absorption intensity at 338 nm (Fig. 5). Absorption spectra of 2-AgNPs with other metal ions did not show any specific change except small reduction of absorption intensity. The concentration dependent studies of 2-AgNPs showed gradual decrease of absorption peak at 415 nm and enhancement of absorption at 338 nm with increasing Pb^{2+} (10^{-6} M) concentration (Fig. S4a). The increase of absorption peak at 338 nm was completed with the addition of 300 µL of Pb^{2+} (10^{-6} M). The interference studies of other metal ions (10^{-3} M) on the selectivity of 2-AgNPs for Pb^{2+} (10^{-6} M) suggest the high selectivity (Fig. S4b). Addition of Pb^{2+} to 2-AgNPs in presence of other metal cations also leads to strong absorption at 338 nm clearly.

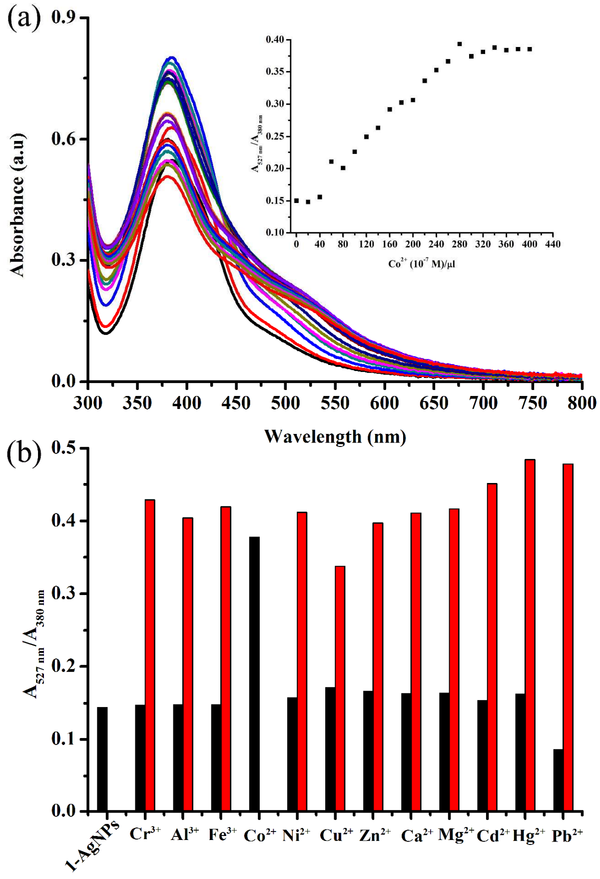


Fig. 4. Change of 1-AgNPs absorbance with Co^{2+} concentration (a) and selectivity studies of 1-AgNPs for Co^{2+} (10^{-6} M) in presence of different metal ions (10^{-3} M).

Rigid diamine based, 3-AgNPs exhibited selective colorimetric sensing of Hg^{2+} ions. Addition of Hg^{2+} into 3-AgNPs resulted in the formation of colourless solution from yellow selectively (Fig. 6). Other metal ions with 3-AgNPs showed only dilution of the yellow color slightly. 3-AgNPs showed SPR absorption at 435 nm and addition of Hg^{2+} lead to complete disappearance of absorption peak (Fig. 6). Absorption spectra of 3-AgNPs with other metal ions slightly reduced the intensity. The concentration dependent studies of 3-AgNPs showed decrease of SPR absorption gradually with blue shift of peak with the concentration of Hg^{2+} (10^{-8} M, Fig. S5a). Absorption peak of 3-AgNPs was completely disappeared with addition of 300 ml of Hg^{2+} (10^{-8} M). The interference studies of 3-AgNPs for Hg^{2+} (10^{-6} M) in presence of various metal cations (10^{-3} M) also confirmed the high selectivity (Fig. S5b).

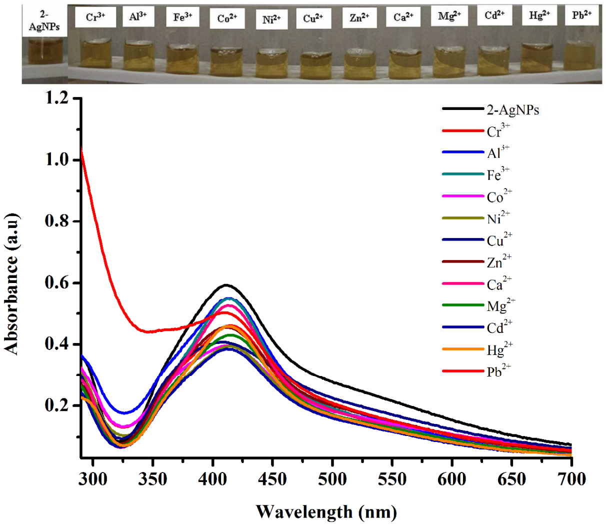


Fig. 5. Absorption spectra and digital images of 2-AgNPs with different metal cations (10^{-3} M).

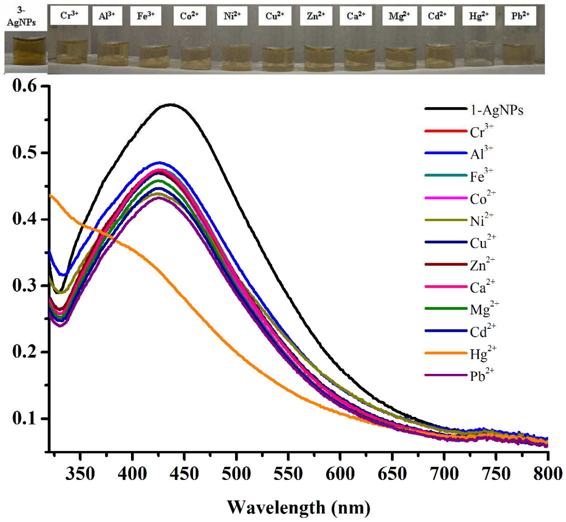


Fig. 6. Absorption spectra and digital images of 3-AgNPs with different metal cations (10^{-3} M).

3.3. Colorimetric sensor studies of anions

1-, 2- and 3-AgNPs has also showed different colorimetric sensing of anions depends on the phenolic chelating ligand. 1-AgNPs showed selective colorimetric sensing of oxalate and dihydrogen phosphate at ppm level. 2-AgNPs did not show any anions colorimetric sensing whereas nitrite ions were selectively detected by 3-AgNPs. 1-AgNPs with oxalate and dihydrogen phosphate showed brownish-pink color formation selectively (Fig. 7). It is noted that oxalate addition produced immediate color change whereas dihydrogen phosphate showed weak orange-pink color initially that was intensified within ten min. Other anions did not show any significant color change with 1-AgNPs. Absorption spectra of 1-AgNPs with oxalate and dihydrogen phosphate clearly showed a new absorption peak at longer wavelength (515 nm, Fig. 7). The intensity of 380 nm peak was substantially reduced. No characteristic change in the 1-AgNPs absorption except small reduction in the intensity was observed with other anions. The concentration dependent studies of 1-AgNPs clearly showed the appearance of longer wavelength absorption with first addition of oxalate (10^{-6} M, Fig. 8a). Further additions only lead to the reduction of absorption intensity at 380 nm that was completed with 240 μL of oxalate (10^{-6} M). The concentration dependent studies for dihydrogen phosphate did not perform due to delayed colorimetric response. 1-AgNPs exhibited good selectivity for oxalate (10^{-6} M) in presence of various anions (10^{-3} M). Addition of oxalate into 1-AgNPs in presence of other anions also showed clear appearance of longer wavelength absorption with reduction of intensity at 380 nm (Fig. 8b). 3-AgNPs exhibited selective decolourisation of yellow colour with nitrite anions. Highly selective sensing of nitrite ions by 3-AgNPs have been recently reported by our group.[54]

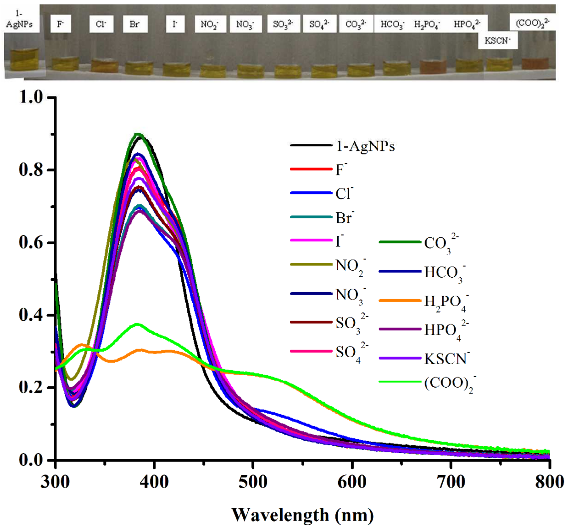


Fig. 7. Absorption spectra and digital images of 1-AgNPs with different anions (10^{-3} M).

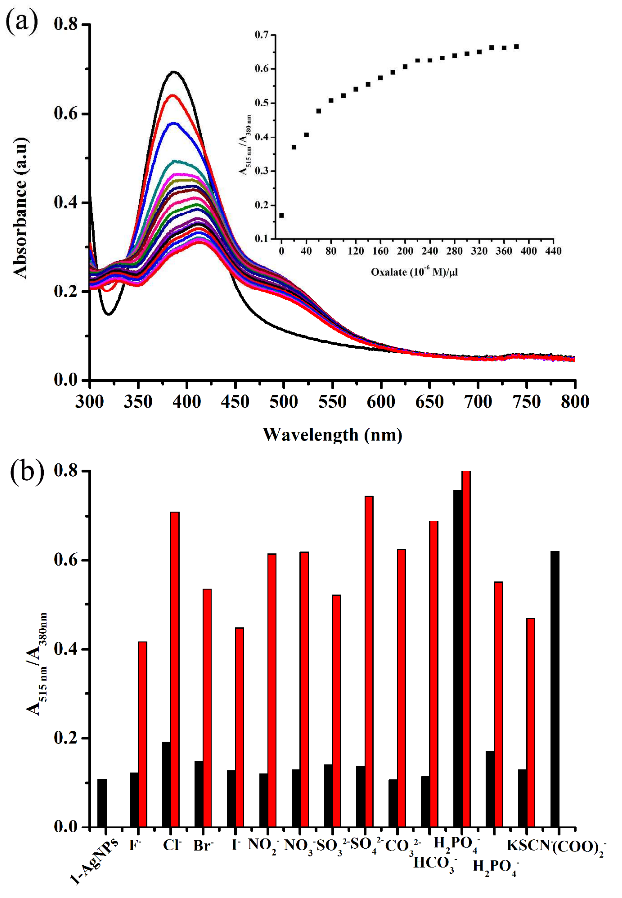
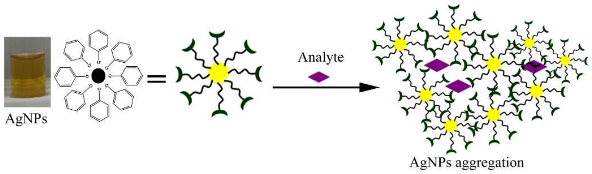


Fig. 8. Change of 1-AgNPs absorbance with oxalate concentration (a) and selectivity studies of 1-AgNPs for oxalate (10^{-6} M) in presence of different metal ions (10^{-3} M).

3.4. Discussion and recovery studies

The selective colorimetric change of 1-AgNPs with Co^{2+}, oxalate and dihydrogen phosphate ions could be due to the aggregation of AgNPs driven by coordination and supramolecular interaction (hydrogen bonding) of anion with phenolic chelating surface functionality of AgNPs. FE-TEM studies of 1-AgNPs with Co^{2+} and anions also confirmed the aggregation of NPs (Fig. 9). Addition of metal cations and anions including Co^{2+}, oxalate and dihydrogen phosphate into aqueous solution of 1 did not show any significant colour formation (Fig. S6a and S7a). This clearly indicates that the colour changes are due to AgNPs aggregation. Absorption studies of 1 with different metal cations were performed to get the insight into the colour change selectively for Co^{2+} (Fig. S8). 1 showed three absorption peaks at 235, 288 and 375 nm. Addition of metal ions increased the absorption intensity with slightly blue or red shifting the peaks position. Interestingly, Co^{2+} addition showed complete disappearance of peak at 288 nm selectively. This indicates the preferential coordination of ligand 1 with Co^{2+}. However, the solution remains clear (Fig. S6a). The selective coordination of Co^{2+} with 1 in presence of AgNPs caused aggregation NPs. 2-AgNPs with Pb^{2+} that showed the precipitate formation did not show any colour change as well as absorption red shift. It only exhibited small reduction in the AgNPs SPR absorption at 415 nm and enhancement absorption at 338 nm. The controlled experiment of 2 with different metal ions showed a clear turbidity formation with Pb^{2+} selectively (Fig. S6b). Addition of different metal cations into aqueous solution of 3 did not show significant change (Fig. S6c). The selective colour disappearance of 3-AgNPs for Hg^{2+} is due to the amalgamation and oxidation of AgNPs to silver ions due to the more positive electrochemical reduction potential of Hg^{2+}.[57] The different selectivity of metal ions arises from the difference in the molecular structure and conformationality. However, the controlled studies 1 with anions did not show any noticeable change (Fig. S7 and S9). This might be due to the weak nature of supramolecular interactions compared to coordination bond. The flexible amine based ligand 1 exhibited clear colorimetric changes for Co^{2+}, oxalate and dihydrogen phosphate ions via coordination and selective supramolecular interaction with surface functionality of AgNPs that caused AgNPs aggregation. The semi-flexible ligand based 2-AgNPs showed selective precipitate formation with Pb^{2+}

without anion sensing. 3-AgNPs that is based on rigid aromatic diamine showed selective decolourisation of yellow for Hg^{2+} cation and nitrite anion colour due to amalgamation and oxidation of AgNPs. The easy oxidation of 3-AgNPs might be due to the weak stability provided by 3.[54] Zeta potential measurement showed that 1, 2 ligand stabilized AgNPs stronger than 3 (Table S1). We have also noticed that AgNPs settles down as precipitate on keeping 3-AgNPs for more than a week whereas 1- and 2-AgNPs were stable for months. Thus the flexible surface functionality of AgNPs plays a important role in the colorimetric sensing of metal cations and anions via coordination or supramolecular interaction induced aggregation. The applications of the 1-AgNPs colorimetric assay for detection of Co^{2+} in presence of different metal cations were also evaluated. As can be seen in Table 1, the mean recoveries of such samples were between 94% and 97% and suggest the potential application of 1-AgNPs colorimetric assay for sensing Co^{2+} ions in water samples.



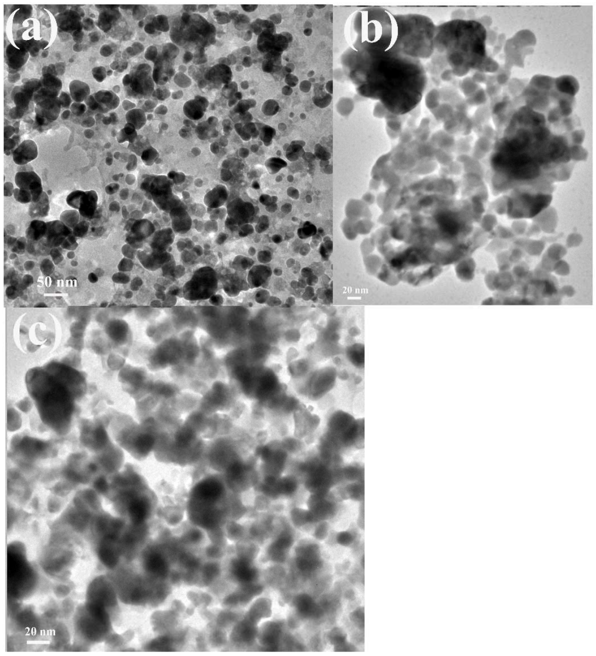


Fig. 9. TEM images of 1-AgNPs with (a) Co^{2+}, (b) oxalate and (c) dihydrogen phosphate.

Conclusion

We have synthesized phenolic chelating ligand functionalized AgNPs and demonstrated ligand dependent colorimetric sensing of metal cations and anions. Highly flexible aliphatic diamine based 1-AgNPs showed highly selective colorimetric detection of Co^{2+} metal ions, oxalate and dihydrogen phosphate anions. Both Co^{2+} and anions (oxalate and dihydrogen phosphate) addition to 1-AgNPs leads to red shift of absorption with clear colour change due to aggregation. However, alicyclic diamine functionalized 2-AgNPs showed selective precipitate formation for Pb^{2+} without exhibiting any colour change. Whereas, weakly stabilized, rigid aromatic diamine functionalized 3-AgNPs showed selective decolourisation of yellow colour for Hg^{2+} and nitrite anions due to amalgamation and oxidation. Thus, subtle structural and conformational change of phenolic chelating ligand could be used for fabricating AgNPs based colorimetric assay for tunable metal cations and anions sensing in water.

Table 1. Determination of Co^{2+} in water samples using the 1-AgNPs colorimetric assay.

Samples	Mean Found (μM)	Mean Recovery[a] (%)	RSD[b] (%)
Co^{2+} (1.0)	0.97	97	0.84
Co^{2+} (1.0)+Hg^{2+}(1.0)+ Pb^{2+}(1.0)+Ca^{2+}(1.0)+Zn^{2+}(1.0)	0.96	96	0.49
Co^{2+} (1.0)+Pb^{2+}(1.0)+ Mn^{2+}(1.0)+Cd^{2+}(1.0)+Ni^{2+} (1.0)	0.94	94	0.86
Co^{2+} (1.0)+Zn^{2+}(1.0)+ Cu^{2+}(1.0)+Mg^{2+}(1.0)+Fe^{3+} (1.0)	0.95	95	1.29
Co^{2+} (1.0)+Ca^{2+}(1.0)+ Pb^{2+}(1.0)+Cd^{2+}(1.0)+Zn^{2+} (1.0)	0.95	95	0.84

[a] Mean recovery (%) =100 x ($\mathbf{c}_{\text{mean found}}/\mathbf{c}_{\text{mean recovery}}$).

[b] Relative standard deviation of three determination.

[c] Values in parentheses=concentration (μM) of the metal ion added.

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Notes and references

School of Chemical & Biotechnology, SASTRA University, Thanjavur-613401, Tamil Nadu, India. Fax: +914362264120; Tel: +914362264101; E-mail: philip@biotech.sastra.edu

† Electronic Supplementary Information (ESI) available: IR, concentration dependent, interference spectra for metal ions and anion sensing by 1-3-AgNPs. See DOI: 10.1039/b000000x/

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