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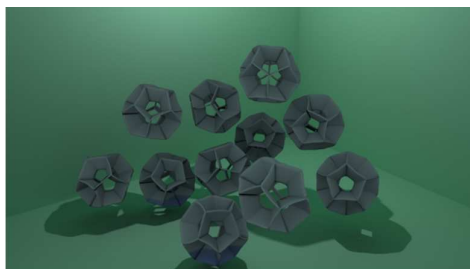
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Graphical Abstract



A gold nanoparticle (Au NP) system based on interaction between cyclam and Au NPs resulted into well defined wheel like supramolecular nanostructures in the presence of Cd²⁺.

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ARTICLE TYPE

Wheel like supramolecular assembly of cyclam decorated gold nanoparticles induced by Cd^{2+} Tanuja Yeluri,^a Namdev V. Ghule,^a Rajesh S. Bhosale,^{a,b} Mohammad Ali Kobaisi,^c Sheshanath V. Bhosale^{*c} and Sidhanath V. Bhosale^{*a}

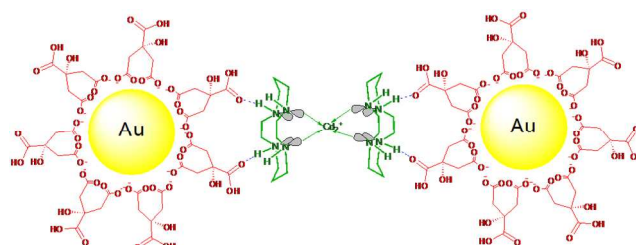
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This study presents a gold nanoparticle (Au NP) system based on interaction between cyclam and Au NPs. We have found that in the presence of Cd^{2+} , cyclam coated Au NPs form well defined wheel like supramolecular assembled nanostructures. Self-assembly is achieved *via* co-ordination bonding between cyclam decorated Au NPs and Cd^{2+} ions. This finding introduces novel assembled nanostructures and contributes to understand the effect of Cd^{2+} cyclam interaction on the morphology of Au NPs assembly.

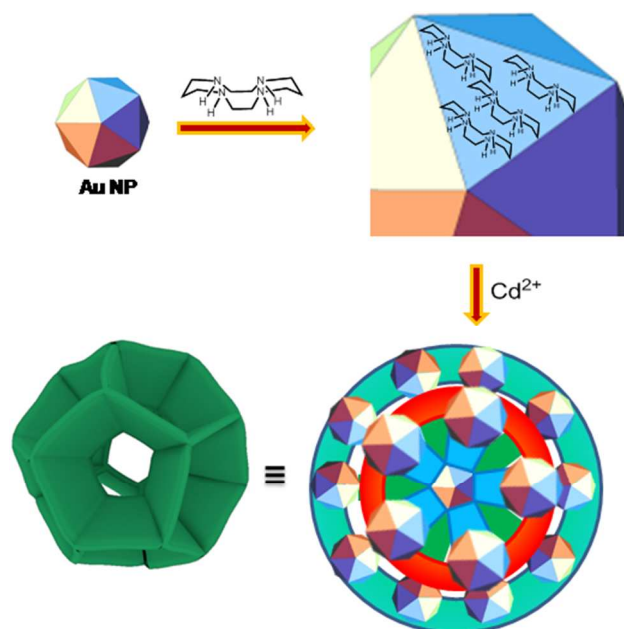
Nanofabrication of material *via* self-assembly of nanosized components has attracted considerable interest because it provides a combination of high throughput and high resolution. Literature survey reveals that the growth mechanism of self-assembled Au NPs using molecular ligands has been reported.¹⁻² Self-assembled material exploiting noncovalent interactions such as electrostatic and directional hydrogen bonding is attractive for several reasons. The development of new methods for the fabrication of controlled self-assembly of Au NPs is of great importance in view of enabling materials with tunable chemical, physical, photophysical, electronic, magnetic and mechanical properties.³ To control self-assembly of Au NPs several approaches have so far been reported based on prefabricated template,⁴ solution deposition methods,⁵ nano-welding,⁶ biomolecular tools,⁷ small molecules⁸ and electrostatic interactions.⁹ These methods offers various pathways towards self-assembly and fabrication of structures of different size, shapes and architectures.¹⁰ The fabricated nanomaterial is employed to the creation of functional nanostructured devices for chemical and biological sensors, light emitting diodes, photodetectors, photovoltaics and scaffolds for biological systems.¹¹⁻¹² Such approaches require a high level of sophistication and synthesis techniques.

Despite the large number of reports describing the self-assembled structures of Au NPs¹³ it is necessary to explore metal directed assembly. In the study, we explored the wheel like assembled nanostructures of cyclam modified Au NPs directed by the interaction of Cd^{2+} ions to the surface bound cyclam (Scheme 1).



Scheme 1 Schematic representation of interaction between Cd^{2+} with cyclam coated Au NPs *via* hydrogen and co-ordination bonding.

Here we assume that cyclam attached to Au NPs surfaces, they may potentially cause strong attractions when the particles approach and make contact with Cd^{2+} . We focus on the influence of various metal ions on the assembly of cyclam coated Au NPs. To the best of our knowledge, this is the first report of wheel like nanostructured morphology by interaction of cyclam modified Au NPs and Cd^{2+} (Scheme 2).



Scheme 2 Schematic illustration for the formation of wheel-like assembly.

Citrate stabilised Au NPs were prepared according to a reported procedure.¹⁴⁻¹⁵ In this protocol, an aqueous solution of hydrogen tetrachloroaurate (HAuCl₄) was added to sodium citrate solution in boiling water bath. The mixture was heated under reflux during this time the color of solution changed from colorless to deep red due to its strong surface plasmon resonance (SPR) absorption. The obtained colloidal particles were analysed by UV-vis absorption and transmission electron microscopy (TEM) used to determine the SPR and the average particle size of the nanoparticles, respectively. The decoration of the Au NPs with cyclam was determined by UV-vis absorption, FT-IR, TEM techniques, and changes were also can be seen by naked-eye. The prepared Au NPs showed plasmon absorption band at 530 nm. This is characteristic of gold nanoparticles (~20 nm) also confirmed with TEM measurements (Fig. S1). In the next step, upon addition of increasing concentration of cyclam to a solution of citrate Au NPs led to decrease in the absorption peak at 530 nm (Fig. 1). However, the peak position and shape of absorbance maxima does not change. Furthermore, naked-eye experiment revealed that the color of Au NPs changed from wine red to violet upon addition of cyclam, and such colour probably due to interaction of cyclam with citrate gold *via* H-bonding (see inset: Fig. 1). Furthermore, the FT-IR spectrum of citrate Au NPs exhibits the characteristic peak for carbonyl of citrate at 1638 and 3393 cm⁻¹ for O-H functional group. We also examined the IR spectrum of cyclam and found peaks at 3187, 3267 and 3422 cm⁻¹ for N-H of ring system. Cyclam coated Au NPs showed bands at 3372 cm⁻¹ (broad) and 1642 cm⁻¹ (C=O), see Supporting Information Fig. S3. This implies that there is hydrogen bonding between N-H of cyclam and oxygen of citrate from Au NPs. However, TEM measurement showed that size of cyclam coated Au NPs is ~20 nm (Fig. S2), which indicates the morphology of such modified particles, remains the same. It is simple surface neutralisation effect *via* H-bonding that is responsible for the cyclam coating on citrate Au NPs.

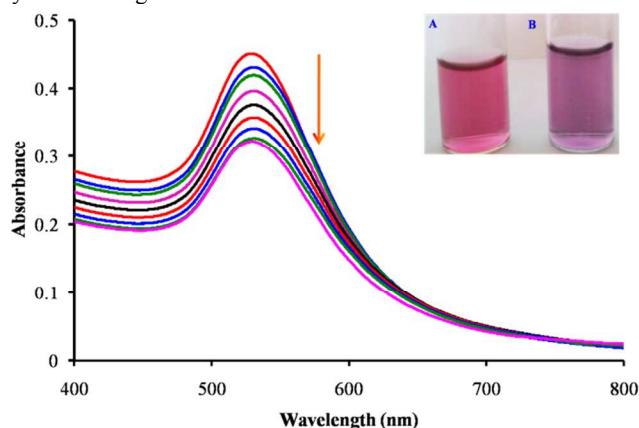


Fig. 1 The UV-vis spectra of Au NPs (0.16 mM) with various concentration of cyclam (0-0.5 mM). Inset: the naked-eye images of Au NPs solution (A) and cyclam decorated Au NPs solution (B).

To demonstrate the assembly of cyclam coated Au NPs different metal cations were added to the aqueous solution of cyclam coated Au NPs. At first glance, the absorption peak at 530 nm was decreased and a strong absorption peak at 670 nm increased, with the addition of increasing concentration of Cd²⁺ ions to the aqueous solution of cyclam Au NPs (Fig. S4). The

bathochromic shift of Au NPs absorption band evolution on aggregation was also examined. Fig. 2 and S4 shows UV-vis absorption spectra for the Cd²⁺ mediated assembly of Au NPs. In the absence of Cd²⁺ such spectral evolution is insignificant. Here, upon addition of Cd²⁺ ions shielding of electrostatic repulsion between Au NPs (electron rich surface) takes place. These results confirm that with the addition of Cd²⁺ in solution, ionic strength increases and the decrease in electrostatic barrier was observed resulted into aggregation of Au NPs yields bathochromic shift in UV-vis spectrum.

Furthermore, by titrating the Cd²⁺ ions quantitative analysis was performed. To quantify the detection limit of the system absorbance measurement was employed. The absorbance intensity of the cyclam decorated Au NPs was decreased at 530 nm with increasing concentration of Cd²⁺. The limit of detection for Cd²⁺ was 0.25 × 10⁻⁶ M (Fig. S5). Upon addition of 12 equivalents of Cd²⁺, the color of cyclam coated Au NPs gradually changed from violet to gray (Fig. S7). With this result in hand we further evaluated the corresponding effect of other metal ions such as Ni²⁺, Co²⁺, Cr²⁺, Mg²⁺, Mn²⁺, Zn²⁺, Cu²⁺, Fe³⁺ and Ba²⁺ and does not found any profound effect on band at 670 nm except Ni²⁺ (Fig. 2a). The absorbance intensity at 670 nm was increased considerably in case of Cd²⁺ and Ni²⁺ (Fig. 2b and Fig. S6). Whereas such significant increase in intensity was not observed in case of other metal ions. Thus UV-vis spectra showed that cyclam decorated Au NPs may undergoes assembly formation in the presence of Cd²⁺ and Ni²⁺. On the basis of our understanding of absorption spectroscopic measurements of citrate Au NPs, cyclam coated Au-NPs and metal mediated titration of cyclam coated Au NPs in aqueous solution suggests that Cd²⁺ and Ni²⁺ binds (co-ordination bonding)¹⁶ to the surface of the Au NPs *via* cyclam (Scheme 1). The Cd²⁺ has high affinity as guest for inclusion complexation with cyclam.¹⁷ Literature survey revealed that for metal coordination to cyclam the best-fit M-N bond length is 2.06 Å.¹⁸ A metal with an ionic radius i.e. 0.65-0.7 Å is related to the stated distance.¹⁸ Smaller metal ions with an ionic radius < 0.75 Å lies in the cavity of cyclam.¹⁹ Whereas those metal ions with increasing ionic strength does not fit the cyclam cavity. Sadler *et al.* reported the crystal structure of Cd²⁺ cyclam complexes.²⁰ They showed in presence of additional chelating agent Cd²⁺ cyclam complex adopt the *cis-I* configuration in which the large Cd²⁺ (ionic radius 0.97 Å) lies above the plane of the ligand. Therefore, we postulate that the Cd²⁺ complexes of cyclam coated on Au NPs are expected to link the individual Au NPs *via* a host-guest interaction as shown in Scheme 1.

Though UV-vis absorption changes of cyclam coated Au NPs are different for different metal ions but the colorimetric sensitivity of these particles for various metal ions is excellent. For individual metal ions color changes of Au NPs are similar to each other regardless of the ion type. This implies that the colorimetric selectivity of cyclam coated Au NPs is very poor for various metal ions (Fig. S7). Therefore we further examined assembly formation of cyclam decorated Au NPs in presence of various metal ions by using TEM techniques to get clear insight.

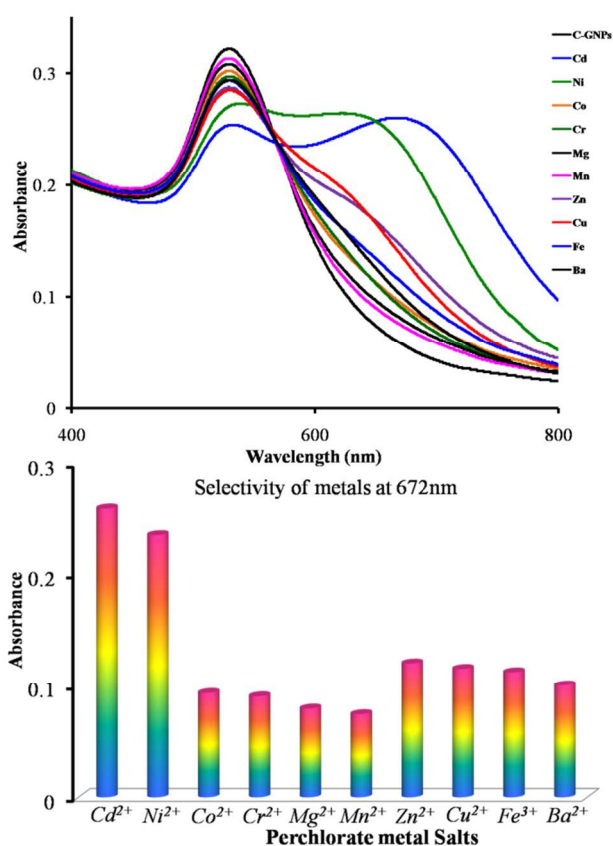


Fig. 2 (A) UV-vis absorption spectra of cyclam-Au NPs in presence of various metal ions (12 equiv.). (B) Absorption intensity at 672 nm of the cyclam Au NPs after addition of different kinds of metal ions.

TEM images acquired by casting a dilute solution of Cd^{2+} induced cyclam coated Au NPs complex on carbon coated copper grids showed the wheel like nanostructured morphology (Fig. 3&Fig. S8). The average diameters for the assembled wheel like nanostructures are about ~ 330 nm. The co-ordinate bonding between Cd^{2+} ions and the cyclam coated on Au NPs can be viewed as spokes of the nanostructured wheels. However, TEM analysis showed that co-ordinate bonding describing the individual spokes cannot be viewed in wheels but it looks like high speed bicycle wheel spinning. This work is confirmation of co-ordinate bonding responsible for wheel like nanostructured assembly (Scheme 1, Fig. 3& Fig. S8). Notably, TEM imaging of Cd^{2+} and cyclam from aqueous solution does not produce any assembly without Au NPs (Fig. S9). This clearly supports the presence of Au NPs leads to formation of wheel like assembly. Furthermore, in presence of Ni^{2+} and other metal ions such wheel like assembly of cyclam decorated Au NPs was not observed. Thus the first supramolecular wheel like assembly of Au NPs was successfully synthesised through a simple self-assembly protocol by utilising Cd^{2+} connectivity via co-ordinate bonding.

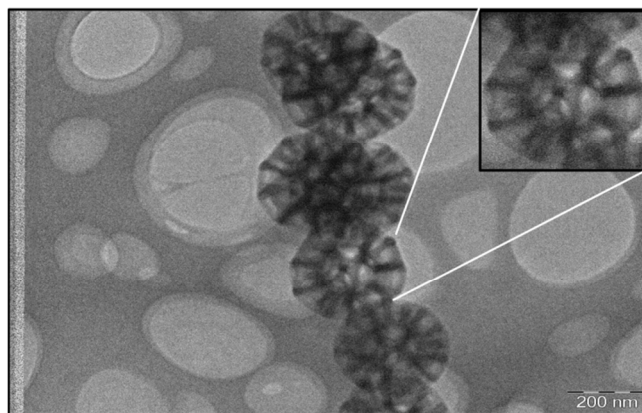


Fig. 3 Wheel like assembly of cyclamAu NPs in presence of Cd^{2+} (Inset shows zoom image of wheel morphology).

In this communication we demonstrated synthesis of cyclam - decorated Au NPs in aqueous solution using non-covalent hydrogen bonding. The interaction between the decorated cyclam on Au NPs with Cd^{2+} ions is believed to be responsible for the interparticle wheel like nanostructured assembly formation. We believe that the constructed self-assembled material is conceptually new one and promises great potential in ion sensing and molecular-scale devices.

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- [†] Electronic Supplementary Information (ESI) available: [UV-vis and TEM measurements]. See DOI: 10.1039/b000000x/
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