Supplementary Information

Wheel like supramolecular assembly of cyclam decorated gold nanoparticles induced by Cd²⁺

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Experimental Section:

1. Materials:

HAuCl₄.3H₂O, cyclam and all metal perchlorates were purchased from Sigma Sigma-Aldrich, Bengalore, India. Trisodium citrate was from analytical rasayana, India. All chemicals were used without further purification.

2. Instrumentation:

The size and the aggregation status of the sodium citrate modified gold nanoparticles were examined by using TECNAI-12, FEI transmission electron microscopy (TEM). Scanning electron microscopy studies were examined by S-3000N HITACHI. UV-vis spectra were recorded on a SHIMADZU UV-vis spectrophotometer. Infrared observations were measured using PERKIN ELMER FT-IR spectrometer.

3. Synthesis of Citrate Gold Nanoparticles. All glassware and magnetic stir bars used in this synthesis were thoroughly cleaned in aqua regia (HCl/HNO₃ 3:1) for 30 min., and then rinsed with milli-Q water, kept in oven at 65 °C for another 1hr. Briefly, An aqueous solution of auric chloride 0.2 mL (50 mM) added to 20 mL of (2 mM) sodium citrate solution was boiled at 100 °C for 15 min under water bath during which time its color changes from colorless to deep red. The solution was then cooled at room temperature followed by centrifugation and redispersion in milli-Q water and the size of the particles was verified through TEM.

4. Preparation of Cyclam Modified Citrate Gold Nanoparticles. The cyclam decorated gold nanoparticles were prepared by adding cyclam to citrate gold nanoparticles such that final concentration of cyclam in the reaction mixture was 0.5 mM, followed by centrifugation (5000 rpm) for 30 min at 25 °C temperature. The prepared particles were redispersed in ultrapure water and wash successively to remove uncoordinated cyclam molecules from solution. The cyclam coated Au NPs clearly differentiate with violet color.

5. Cd^{2+} -cyclam modified Nanoparticles Assemblies: UV-vis spectroscopic titrations were employed to investigate assemblies of gold nanoparticles. Take 2.5 ml of cyclam decorated gold nanoparticles in milli 'Q' water and used for titration in presence of various metal ions. Titration of cyclam coated Au NPs were performed at room temperatures in presence of each metal ions $1x10^{-2}$ M (0-12 equiv.).

6. Transmission electron microscopy: Transmission electron microscopy (TECNAI-12, FEI operating voltage 200 kv, on resolution 2.4 Å) was employed to investigate the morphology of the Au nanoparticles, cyclam decorated Au NPs and metal induced assembly structures. In this protocol droplets of the aqueous solution (ultrapure) of all three samples were placed onto carbon-coated copper grid and were left to dry for 30 min. All air dried samples studied were subjected for further visualization of morphology and self-assembly structures.

7. Supporting figures:

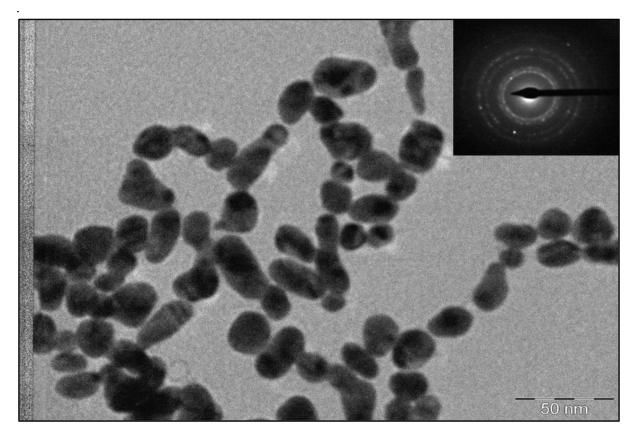


Fig.S1 TEM images of citrate gold nanoparticles (inset shows diffraction pattern)

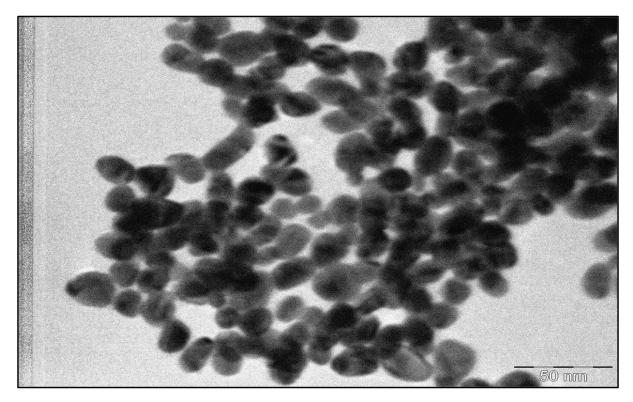


Fig.S2 Cyclam modified citrate gold nanoparticles.

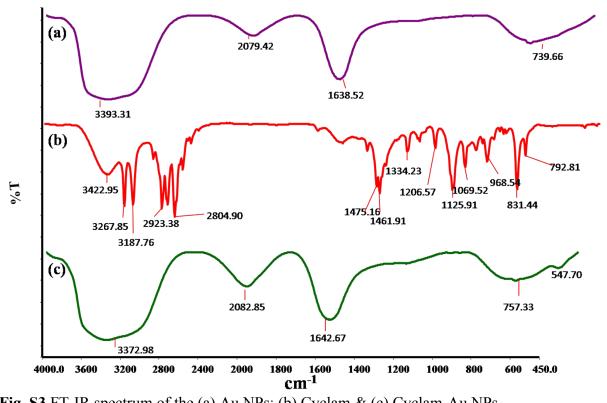


Fig. S3 FT-IR spectrum of the (a) Au NPs; (b) Cyclam & (c) Cyclam-Au NPs.

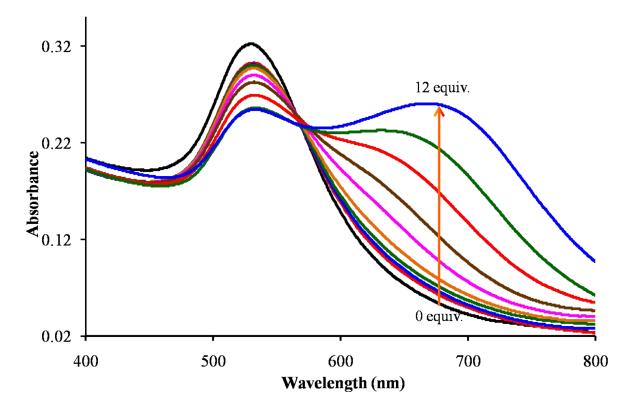


Fig. S4 UV-Vis absorbance spectra of cyclam-coated Au NPs titrated with Cd²⁺ ion (0-12 equiv.).

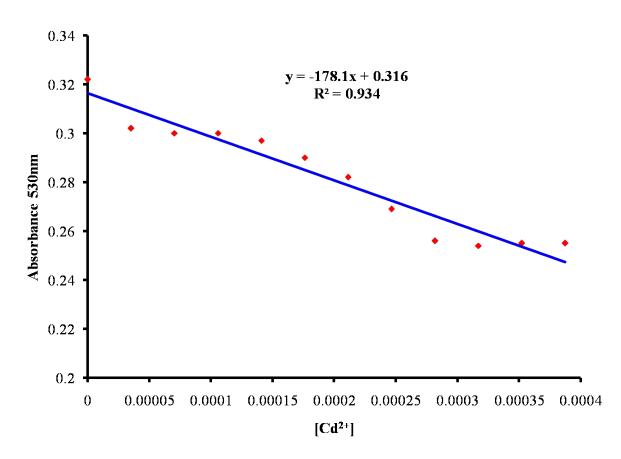


Fig.S5 Limit of detection of Cd²⁺ Metal ion with cyclam Au NPs.

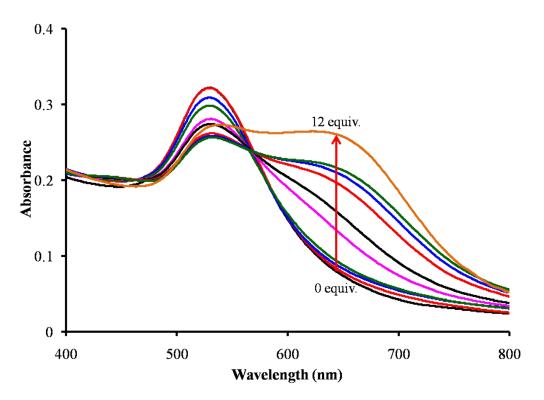


Fig. S6 UV-Vis absorbance spectra of cyclam-coated Au NPs titrated with Ni^{2+} ion (0-12 equiv.).

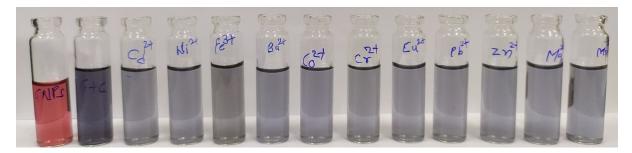


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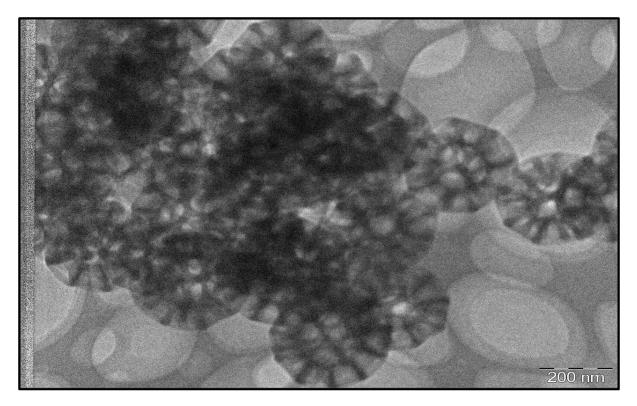


Fig.S8 TEM images of sodium citrate modified GNPs (0.16 mM) in presence of cyclam (0.5 mM) & Cd²⁺ ion (12 Equiv.).

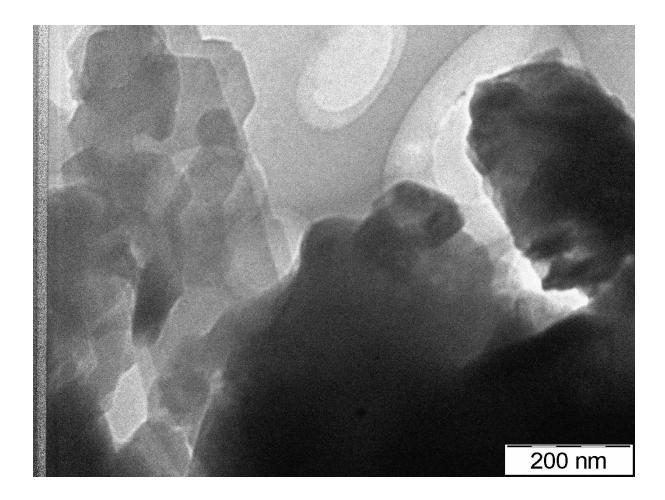


Fig.S9 TEM picture of cyclam-Cd²⁺ complex.