

ADVANCED MATERIALS

Supporting Information

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ONLINE SUPPORTING INFORMATION FOR:

Self-Assembly of Microns Long One Dimensional Network of Cemented Au Nanoparticles

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SUPPORTING INFORMATION

I: Reagents & Instruments:

All reagents except for Au nanoparticles are purchased from Sigma-Aldrich and used without further purification. Distilled water filtered with Millipore 0.22 μ m filters (resistivity > 18M Ω cm) is used for all synthesis reactions. Au 10 nm particles with anionic citrate functionality are purchased from BBI international.

UV-visible absorption spectra are recorded in an ocean-optics absorbance spectrophotometer equipped with 10 mm quartz cuvette holder for liquid sample. TEM analysis is performed in a Hitachi-H-9000 NAR and the samples are prepared by placing a drop of fresh solution on Carbon film coated Copper (Cu) grids, followed by immediate removal of the excess solvent using a blotting paper. Photo-Luminescence spectra are recorded on a Hitachi spectrophotometer, F-4500.

Safety

It should be noted that Cadmium salts are carcinogenic and should be handled with proper care and precautions.

Methods

A pH 6 solution of 10 nm Au nanoparticle of concentration 5.7×10^{12} particles/ml is purchased from BBI International. These particles are prepared by citrate reduction, resulting in citrate ions being absorbed on the Au surface making them negatively charged. The UV-Vis spectrum shows the well known surface plasmon resonance (SPR) absorption band at ~ 525 nm (Au curve in Fig S5). Cadmium perchlorate hydrate solution of concentration 1 mg/ml (Cd solution) is separately prepared and sonicated for 2 hours and added drop wise to Au solution under constant stirring at a volume ratio of 1:4. The solution is allowed to stir for 12 hrs. The color of the solution is transformed from wine red to violet-blue that corresponds to a shift in the SPR band from 525 nm for Au nanoparticle solution to ~ 620 nm with a shoulder at 525nm (Au-Cd curve in Fig S5). A 1 mg/ml solution of PSS (molecular weight 500,000 Dalton) is made and stir for 4 hours. 200 μ l of PSS solution is added to the Au/Cd solution and allowed to stir overnight. No significant change in absorbance spectrum is observed except for the appearance of the PSS absorbance at 265 nm. Following this Na_2S is added to the solution in 0.7 times the stoichiometric ratio with respect to Cd in dark. The absorbance spectrum changes significantly (curve PSS-CdS-Au in Fig. S5). The complete synthesis is done under inert nitrogen conditions.

Energy Dispersive X-ray Analysis (EDX), elemental analysis is performed on the cemented necklace with a 60 nm beam spot size. The spectrum shows presence of Au and CdS in the cemented necklace (Fig S7). The Cu peak is due to the Cu grid used for sample preparation and the Cr peak is due to the sample holder of the TEM instrument.

Electrical measurement is done on Au electrodes 50 μ m apart on SiO_2/Si chips. The cemented material (PSS-CdS-Au) is deposited by electrostatic attraction to oppositely charged surface (Cationic functionalized). The presented current-voltage results at different temperatures are from the same sample, hence requiring no normalization for comparison. Similar qualitative results are obtained from other samples made with identical procedure.

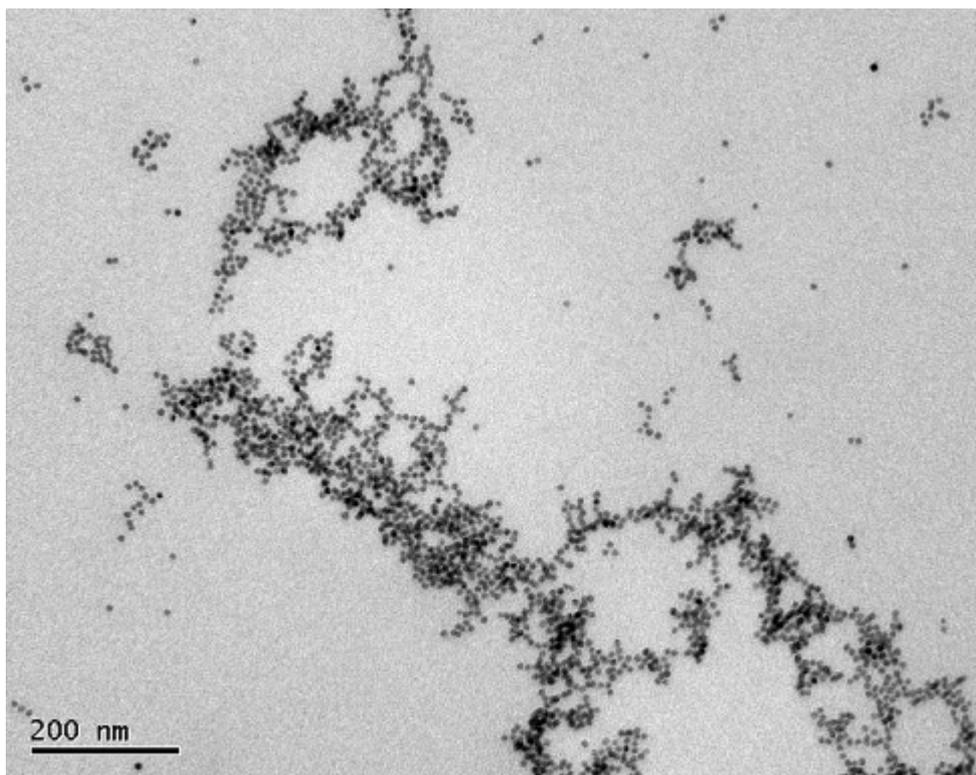


Fig S1. TEM analysis of the Au-Cd assembly. Clustered assembly of Au nanoparticles with string like morphology is observed.

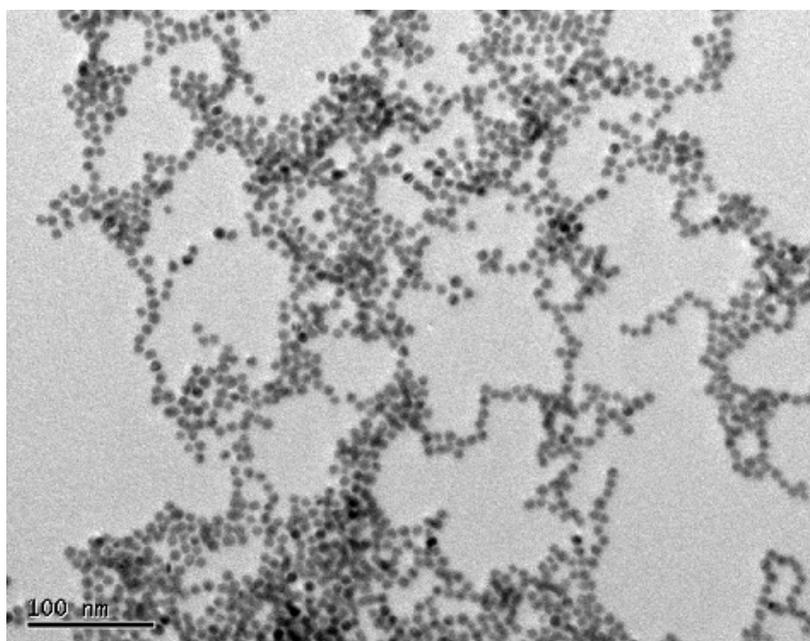


Fig S2. TEM analysis of the Au-Cd assembly. Clustered assembly of Au nanoparticles with string like morphology is observed.

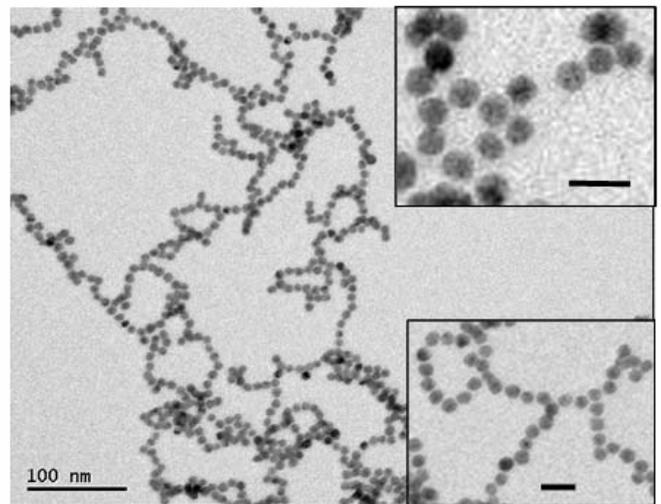
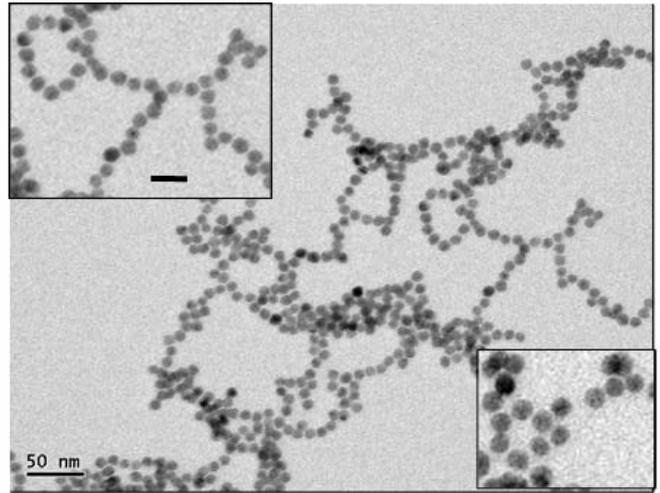
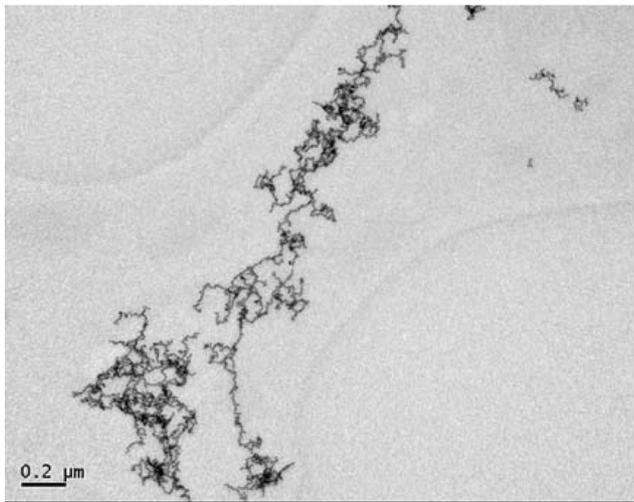


Fig S3. TEM analysis of the 1-D branched assemblies of discrete Au nanoparticles resulting from the PSS-Cd-Au interaction. The inset scale bars are 20 nm.

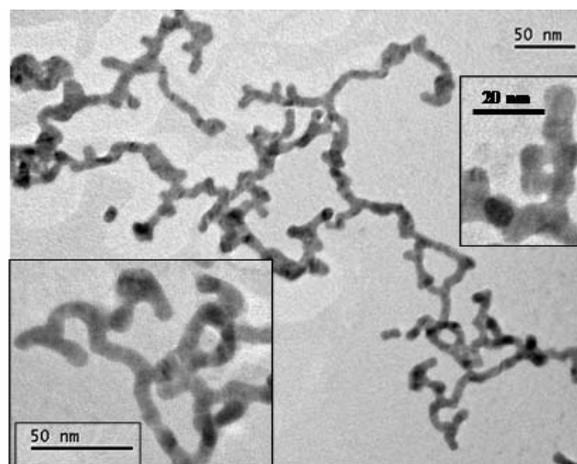
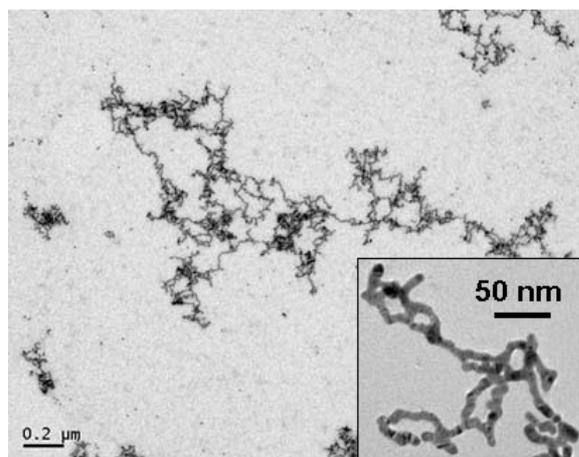
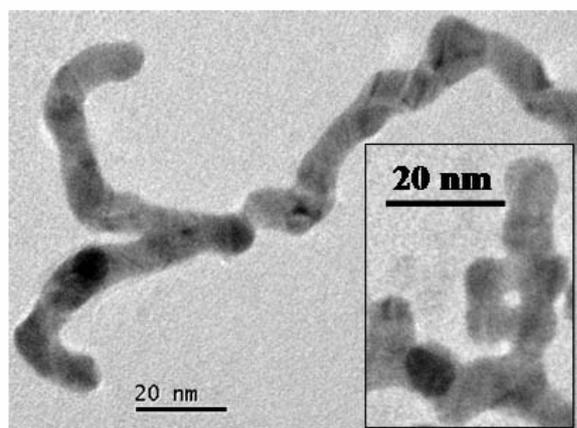


Fig S4. TEM analysis of the transformed assembly. On addition of Na_2S the discrete Au nanoparticles of fig S-3 are transformed to a continuous structure.



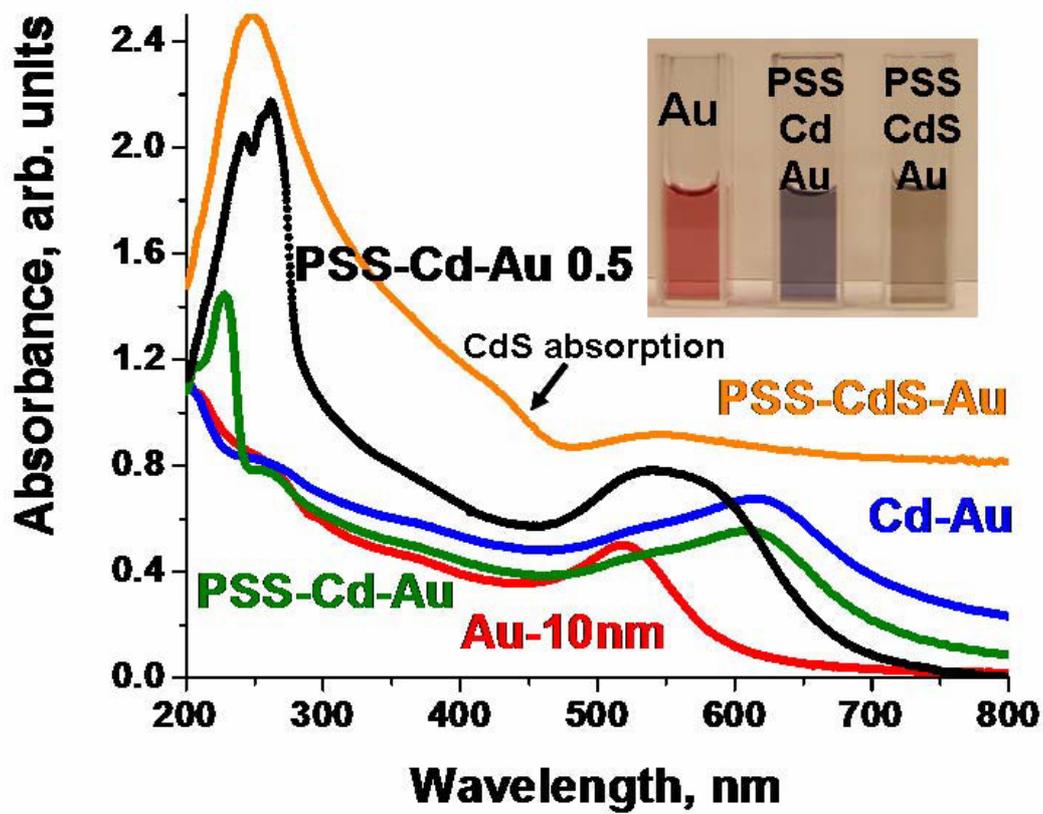


Fig S5. Absorption spectra of the synthesis at each stage of transformation. The PSS-CdS-Au spectrum has been shifted vertically for better visualization. The change in the color of the solution from wine red to violet blue and to muddy yellow is visible in the photograph

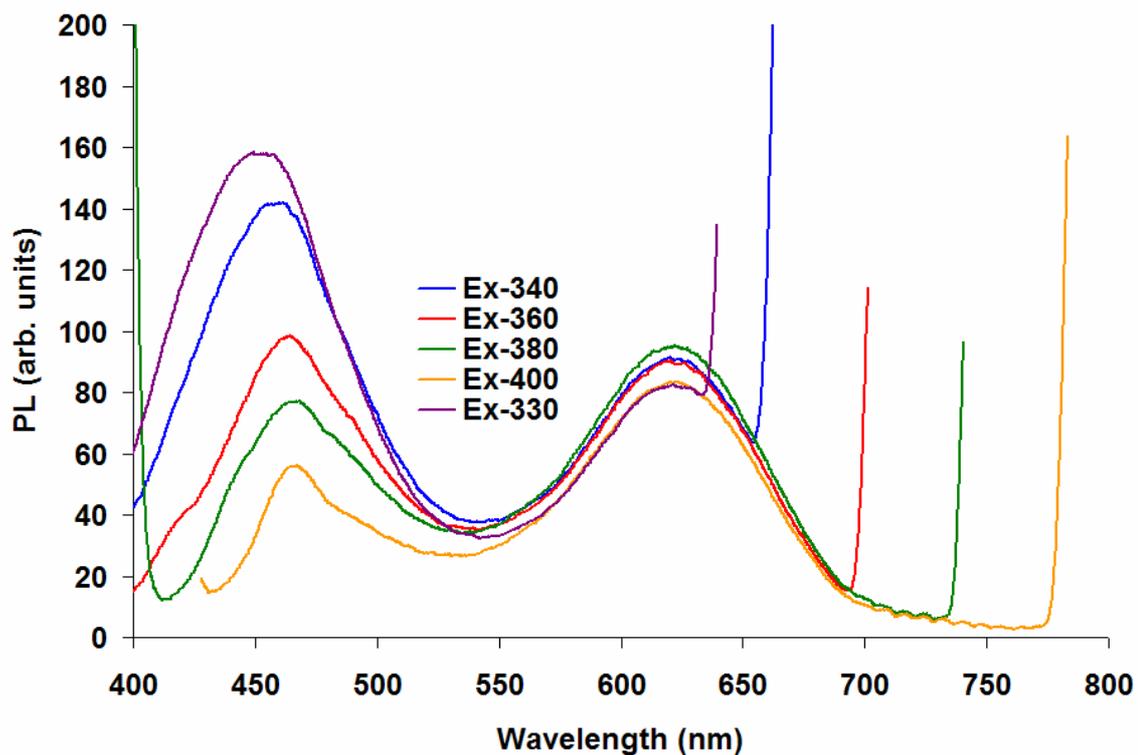


Fig S6. Photoluminescence emission spectra of the PSS-CdS-Au, 1-D branched continuous assembly. A new emission peak at 620 nm appears on addition of Na_2S , due to formation of CdS. Inset shows the spectra for PSS-Cd-Au assembly, showing only the Au nanoparticle peak. A similar spectrum is shown by Au nanoparticles.

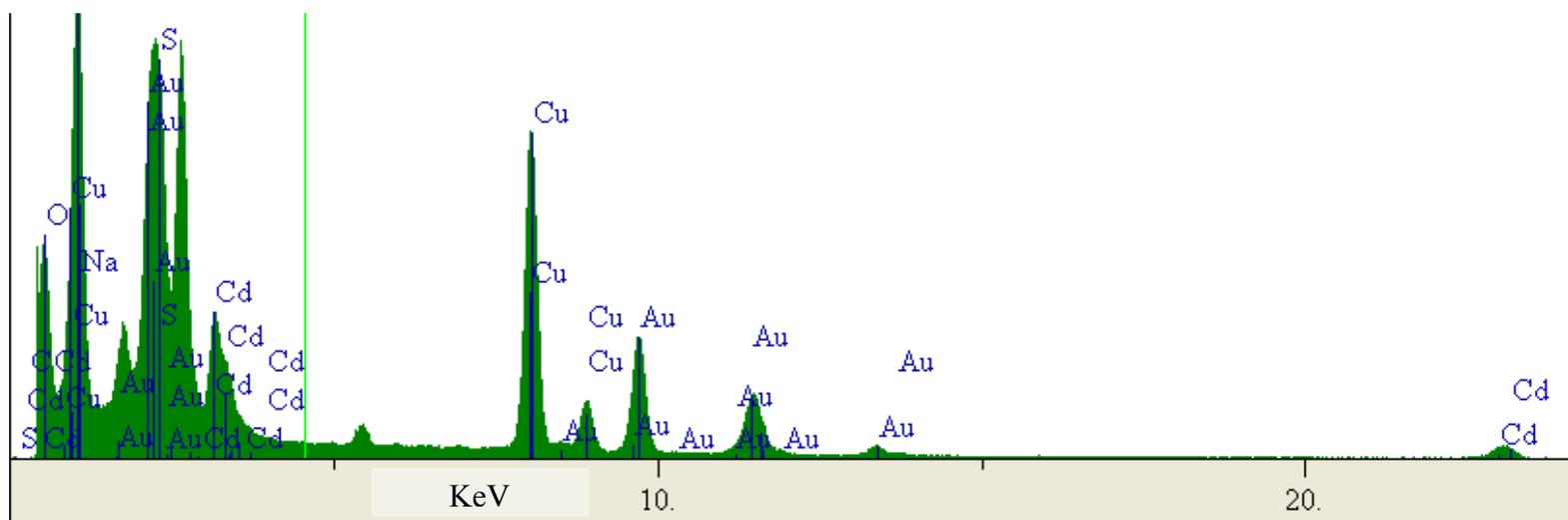


Fig S7. EDX spectra of the PSS-CdS-Au, 1-D branched continuous assembly. The collection is done using a 60 μm beam spot size. The analysis shows the presence of Au, Cd and S in the assembly. The Cu peak is due to Cu grids used for making the TEM sample. The peak at ~ 5.7 KeV is due to Chromium, the material of TEM sample holder.

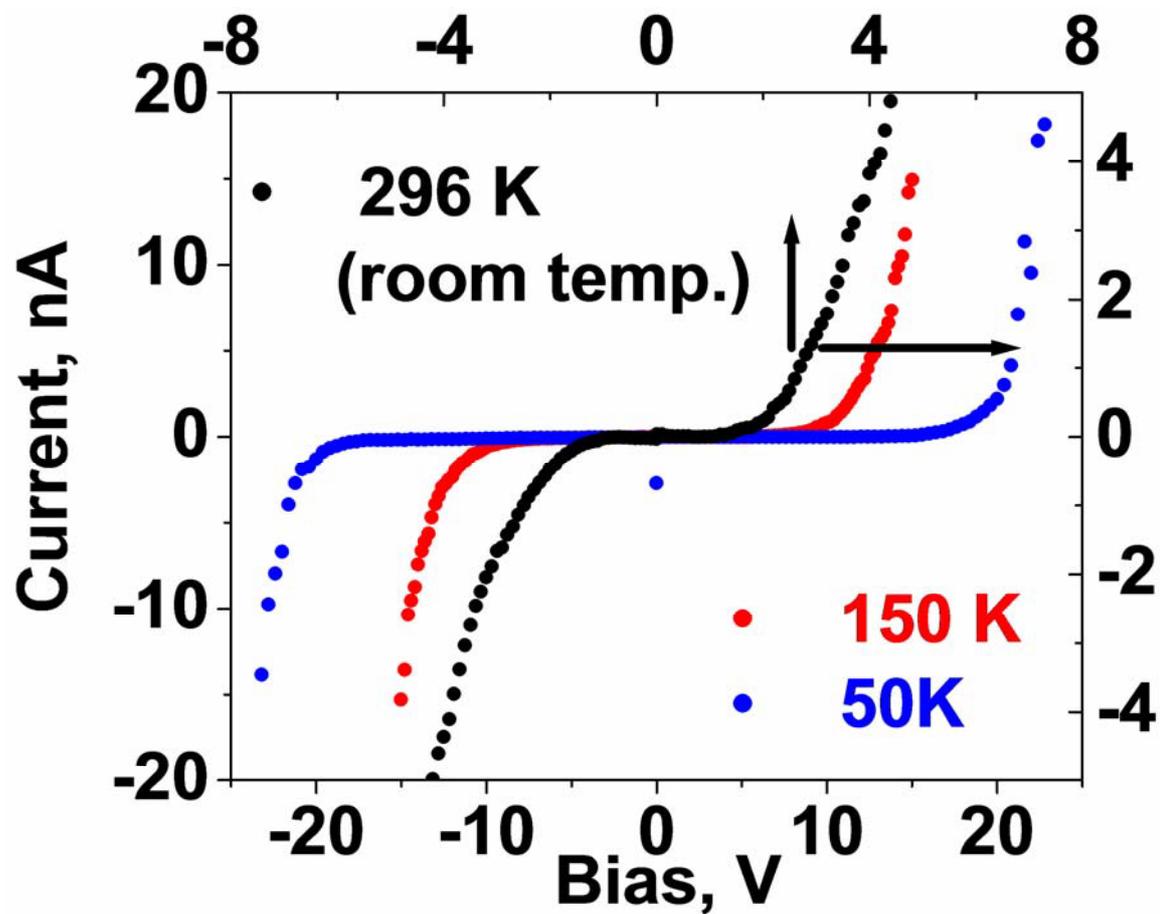


Fig S8. Electrical measurements of the PSS-CdS-Au, 1-D branched continuous assembly deposited between Au electrodes, 50 μm apart. Remarkably high coulomb blockade is observed even at room temperature. The magnitude of blockade increases with temperature.

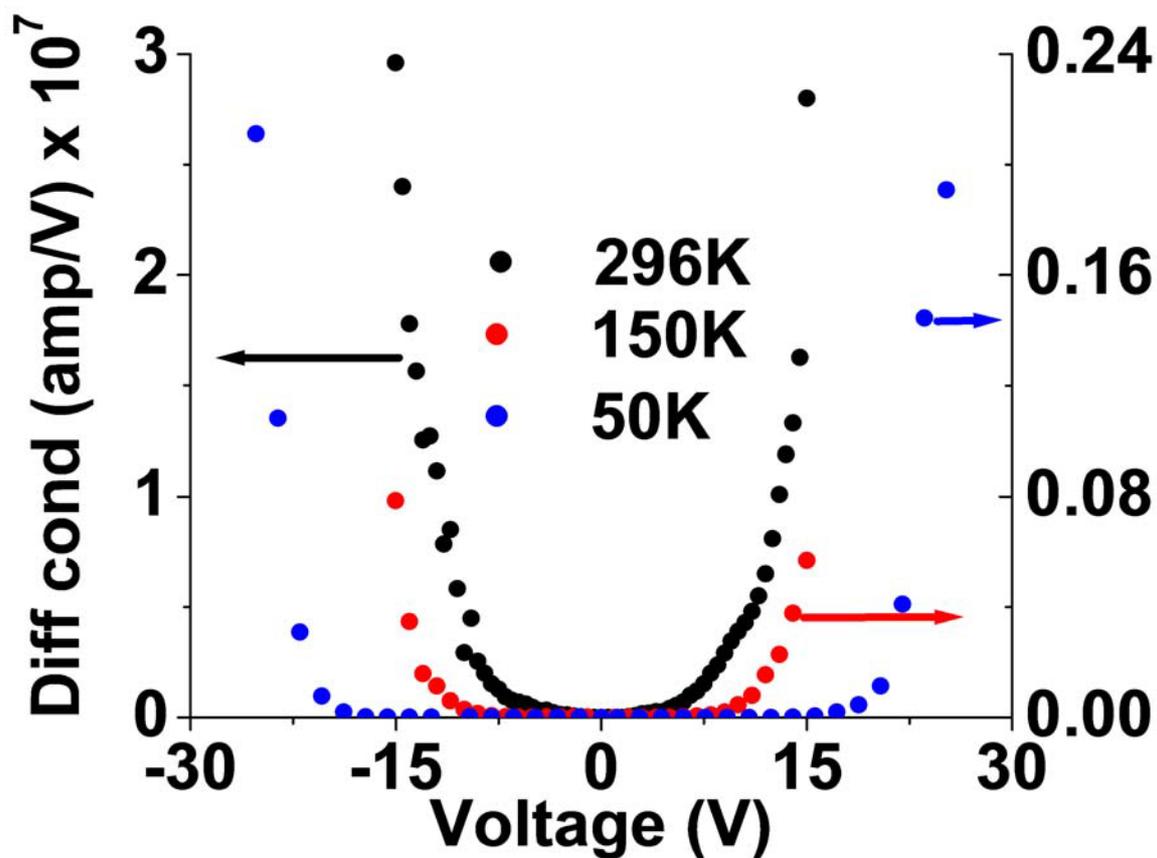


Fig S9. Differential conductivity plots from electrical measurements of the PSS-CdS-Au, 1-D branched continuous assembly deposited between Au electrodes, 50 μm apart. Remarkably high coulomb blockade is observed even at room temperature. The magnitude of blockade increases with temperature.