Supplementary Information (SI) for Nanoscale.

Methods

Materials (reagents)

$HAuCl_4 \cdot 3H_2O$, trisodium citrate, $NaBH_4$, 4-MBA, $Cu(NO_3)_2 \cdot 2.5H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and are used as received. Deionized (DI) water is obtained in-house (18.2 MOhm cm^{-1} at 25 °C).

Citrate-Capped Au Nanoparticle Synthesis

C-NPs ~ 5 nm in diameter are prepared following a modified Turkevich method [1,2]. 12 mL of 38.8 mM trisodium citrate aqueous solution is added to 150 mL of 1 mM $HAuCl_4$ aqueous solution and stirred for 5 min. 4.5 mL of 100 mM $NaBH_4$ aqueous solution is then added dropwise under vigorous stirring, immediately causing the reaction to turn red and indicating the formation of C-NPs. The C-NP solution is allowed to age for 24 h before use to allow excess $NaBH_4$ to decompose.

Ligand exchange : MBA-Capped Au Nanoparticles

A 13 mM, MBA aqueous solution is prepared, adding NaOH until MBA dissolves fully. 1 mL of 13 mM MBA solution is added to 150 mL C-NP solution prepared above, and the mixture is stirred for 2 h at room temperature (~22 °C) to allow ligand exchange to occur [3].

pH selective precipitation is used to remove excess citrate and MBA ligands. The pH is lowered to ~ 2 using dilute HCl to protonate MBA, inducing hydrogen bonding between NPs. The solution is centrifuged at 2400 RPM for 10 min to precipitate the NPs. The supernatant containing excess ligands is discarded, and the MBA-NP aggregate is washed with deionized water, keeping the pH below ~ 2 so that the NPs remain aggregated. The washing and centrifugation steps are repeated two additional times. Finally, the purified MBA-NPs are redispersed in deionized water using dilute NaOH to raise pH to ~ 9. The solution is stored at 4 °C.

Ion-doped NP aggregates

Macroscopic quantities of ion-doped- NP aggregates are fabricated by mixing 150 mL of NP solution with 1.5 mL of 300 mM (C-NPs) or 30 mM (MBA-NPs) metal ion aqueous solutions under gentle stirring for ~1 min. Crosslinking leading to aggregate formation occurs rapidly and can be visibly observed by a colour shift from red to blue [4]. Nanostructured aggregates precipitate from the solution on their own over ~12 h. When precipitation is completed, the supernatant is removed, and the aggregates are rinsed with DI water 5 times and then dried under vacuum for 1 h.

Magnetic Measurements

Magnetic measurements are obtained using a Magnetic Property Measurement System (MPMS-3, Quantum Design) down to 2 K following slightly different procedures for the C-NPs and MBA-NPs. C-NP aggregates are mounted on a low background quartz paddle using GE varnish, while MBA-NP aggregates are placed in a gel capsule which is held inside a straw. C-NPs are pumped for 12 h to reduce trapped air; nevertheless, some oxygen remains trapped as evidenced by an O_2 signal observed near 80 K in all M vs T data for C-NP samples. M vs T measurements are obtained by cooling in a 500 Oe external field.

Thin Au films and Charge Transport Measurements

Glass slides microscope slides are cleaned by sonication in methanol and acetone for 10 min, and then immersion in boiling piranha (3 : 1 H_2SO_4/H_2O_2) for 30 min. Five Au electrodes (50 nm thick Au on 5 nm Ti adhesion layer, 1 mm x 2 mm footprint area, ~ 1mm separation) are thermally deposited on the slides. Next, an Au film (8 nm thick with 5 nm adhesion layer) is deposited on top of the electrodes. Indium solder is used to attach magnet wires to each electrode, and solder joints are covered with Torr-seal epoxy and cured at 100 °C for 1 h. A self-assembled monolayer (SAM) is formed on the Au film by immersion in 1 mM ethanolic MBA solution for 13 h. Finally, Cu^{2+} is bound to the MBA SAM by immersion in 3 mM Cu^{2+} nitrate aqueous solution for 13 h.

Samples for CV measurements employ a single Au electrode (50 nm thick Au on 5 nm Ti adhesion layer) across the entire substrate. Remaining fabricated steps are as described above.

Four-probe resistance (R) vs. temperature (T) behaviour is measured at each step of the sample fabrication process (bare Au film, Au film / SAM, and Au film / SAM / ion) using a He-4 cryostat and an AC resistance bridge.

Characterization

UV-Vis measurements are conducted using an EMC-11-UV spectrophotometer with a Tungsten filament. TEM Images are obtained using a Hitachi HT7700 TEM operated at 100 kV acceleration voltage. TEM samples are prepared by drop-casting NP solutions on a TEM grid and allowing the solvent to evaporate.

CV of MBA self-assembled monolayers are performed using a home-built 3-probe electrochemical cell with 0.1 M phosphate buffer (pH 7.4) as an electrolyte (degassed with argon), and platinum mesh as the counter electrode. A silver wire immersed in 3.0 M KCl solution is used as an Ag/AgCl reference electrode. For further details of this electrochemical cell see [5].

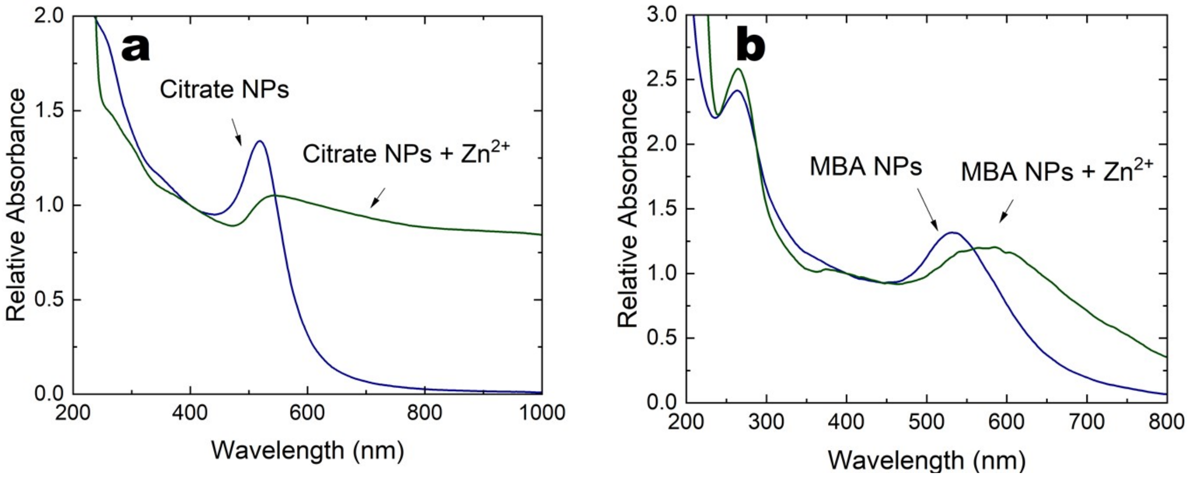

Figure S1: UV-Vis spectra of C- and MBA- NPs in solution before and after addition of Zn^{2+} ions. Spectra taken 1 minute after addition of ions to highlight the immediate impact these ions have to aggregate Au NPs.

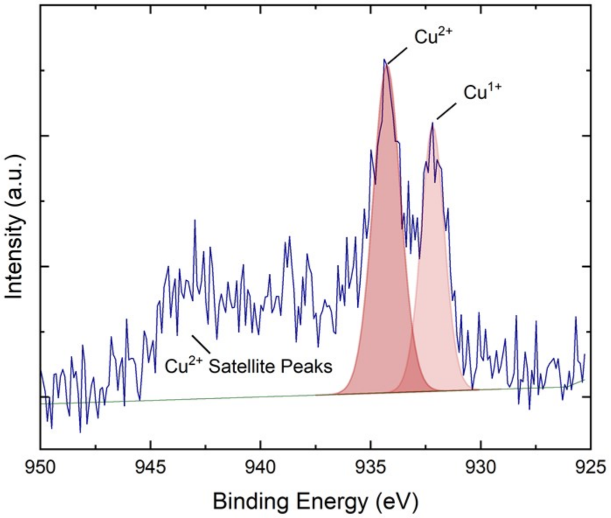

Figure S2: XPS spectra of the Cu 2p region for Cu^{2+} doped MBA - NP aggregates. Peak fitting yields a Cu^{2+} dopant concentration of approximately 1.7%.

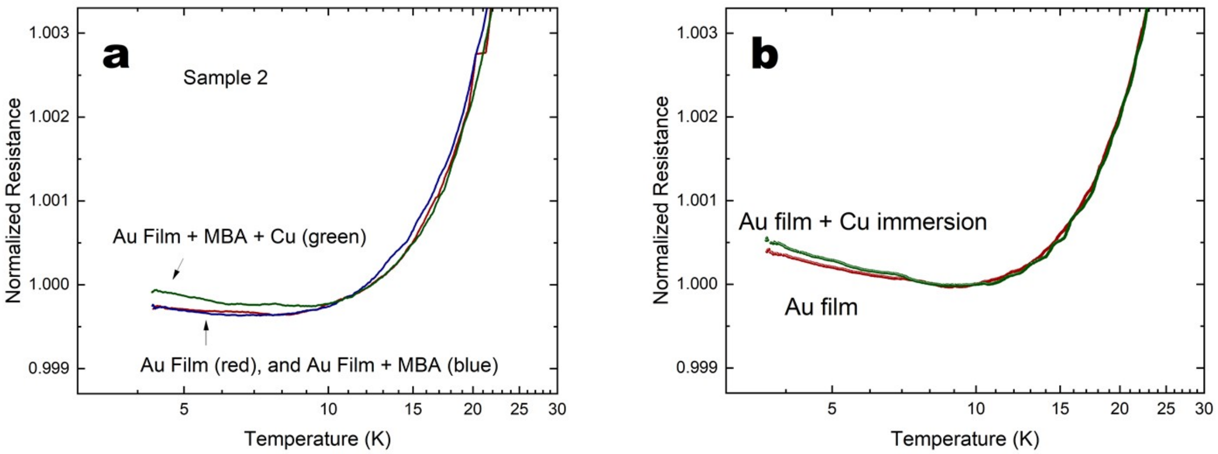

Figure S3: Additional *R* vs *T* samples. a) Additional Cu^{2+} doped sample showing similar characteristics to sample shown in main paper. *R* vs *T* of a single Au film at different stages of Cu^{2+} doping: bare film (red), after depositing an MBA SAM (blue), and subsequently doping with Cu^{2+} (green). A resistance increase only after Cu^{2+} immersion is apparent below 10 K. Here we normalized all data to 11 K. b) *R* vs *T* of a single Au film at different stages of Cu^{2+} doping <u>without</u> MBA monolayer growth: bare film (red) and subsequently immersing film in Cu^{2+} (green). Here the resistance upturn is small compared to the original bare Au film.

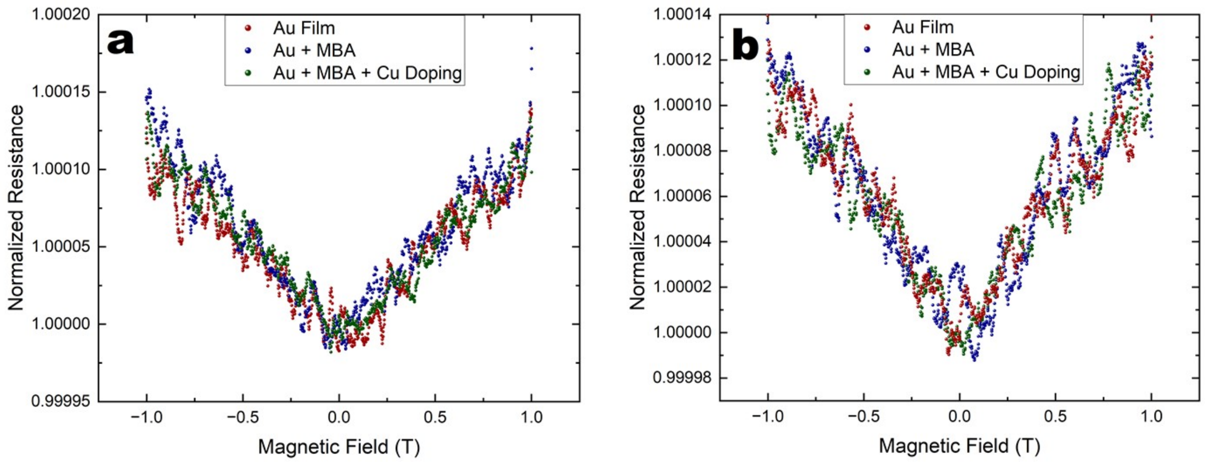

Figure S4: Magnetoresistance measurements of Cu^{2+} doped MBA monolayers on two thin 8nm Au films at each step of film preparation.

References

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[2] W. Haiss *et al.*, Anal. Chem. **79**, 4215 (2007).
[3] Y. Zhou *et al.*, Colloids and Surfaces A: Physicochemical and Engineering Aspects **391**, 179 (2011).
[4] S. Colford and A.-A. Dhirani, Colloids and Surfaces A: Physicochemical and Engineering Aspects **723**, 137416 (2025).
[5] X. Chen and A.-A. Dhirani, ACS Appl. Mater. Interfaces **16**, 25540 (2024).