Electronic Supporting Information for:

Surface mediated assembly of small, metastable gold nanoclusters

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Materials and Methods

Plating Bath Preparation for scaled process. We have developed a synthesis solution that can be dried and stored for over a month, redispersed in clean solvent, and subsequently deposits gold clusters in less than 1 h. The solution is prepared by stirring $AuClPPh_3$ (maximum mass examined was 300 mg) into 45 mL of pure ethanol in a 50 mL crimp seal vial.[1] After 15 min of stirring, the addition of ≈4.5x molar excess of dry $NaBH_4$ (Sigma-Aldrich, 99%) is added to the $AuClPPh_3$ solution, the solution is sealed, and then shaken vigorously. The solution is allowed to react for 6 days to allow the evolution of the initially broad gold cluster distribution.[2] Subsequently, the reaction solution is added to 250 mL toluene to precipitate the gold nanoclusters. The entire solution is centrifuged for 45 min at 2000 rpm. The supernatant is decanted, and the clusters are washed with methanol, 3:1 methanol-chloroform, 2:1 chloroform, and subsequently dried in a desiccator. The dried plating residue is stored in a screw top vial. To initiate plating, the solution is resuspended in clean solvent, and the substrate is placed vertically in the plating bath is to minimize impurities in the thin-film. The scalable plating solution does contain larger cluster "impurities". The dried mixture initiates film formation in < 1 h when resuspended in clean solvent.

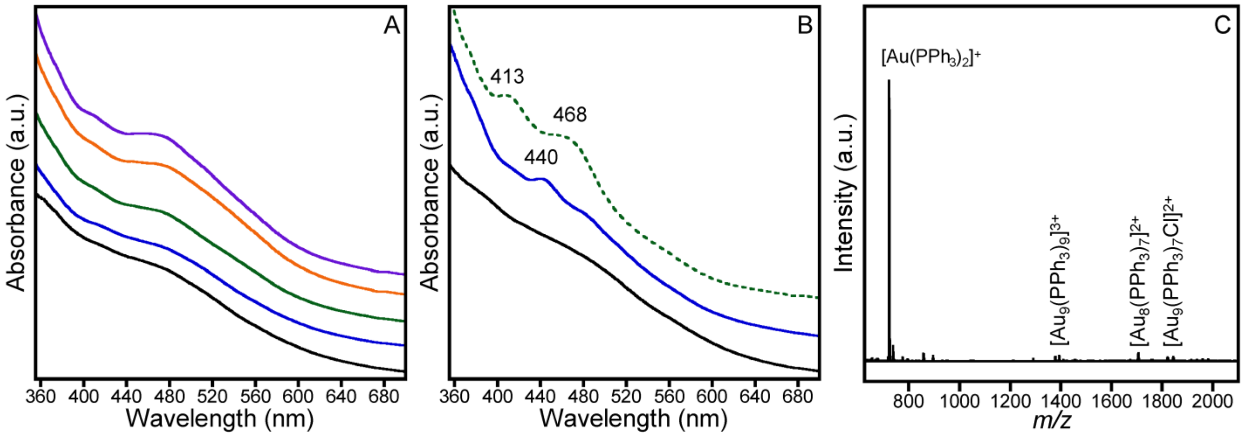

Figure S1. A) Unassayed solutions of $AuClPPh_3$ reduced with BTBC in methanol-diethyl ether mixtures (1:1, v/v) as function of increasing time, where the spectra are offset for clarity. The broad absorbance initially observed (black trace) remains during plating, which does not allow the distribution of nanoclusters present to be identified or quantified. B) Plating solution prepared by reducing $AuClPPh_3$ with $NaBH_4$ in a methanol-chlororfom mixture (1:1, v/v). Because the PPh_3-protected products are more soluble in the chloroform mixture, increasing populations of the $[Au_9]^0$ depositing species can accumulate prior to onset of deposition, which is observed with the increasing intensity of the 440 nm band (blue trace) from the broad absorbance initially observed during Stage I (black trace). After completion of deposition, absorbance bands at 413 nm and 468 nm are observed in UV-Vis spectrum, which are characteristic PPh_3-protected Au_8 clusters and indicates these species are not preferentially co-depositing with the $[Au_9]^0$. C) ESI-MS spectra of the methanol-chloroform solution from Figure 1A after deposition displaying the persistence of theoretically stable, ionic, PPh_3-protected Au_8 and Au_9 clusters. The relative intensity of the ionic Au_8 and Au_9 clusters did not change significantly during any stage of deposition.

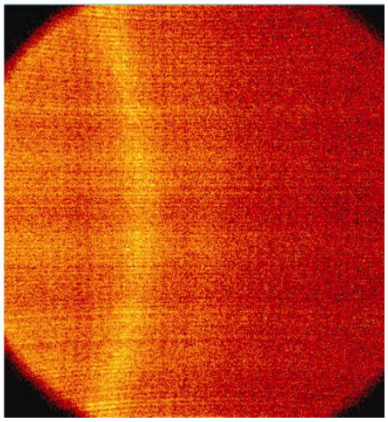

Figure S2. Representative intensity map collected on the area detector showing a continuous band, which indicates the absence of texture in the film.

DDT processing

Data supporting distinct structure in the sub 3 nm assemblies are also observed in the presence of excess DDT (Figure S3). Submerging the films in a hexane solution containing ≈ 2× molar excess DDT produces a red solution which is similar to those observed in the L^3 systems. The UV-Vis spectrum is again similar to synthesized, bare ≈3-4 nm Au particles (Figure 5, top panel). However, in the presence ≥ 3× molar excess DDT, the film initially displays the red color, but the gold species are completely dissolved within 24 h to 48 h resulting in a clear solution. This is not unexpected if small nanocluster are present in the crystalline assemblies, because alkanethiols are not reported to be efficient stabilizers of small Au_x nanoclusters, where $x < 13$. The nanoparticles with the same optical signature to the liberated gold assemblies did not dissolve in the presence of similar excess DDT. Furthermore, increasing excess amounts of thiols are commonly used in a broad number of gold nanoparticle syntheses to trap and stabilize small nanoparticles.[42] Because the dissolution of the films in the presence L^3 results in the reappearance of nanoclusters and completely dissolves in the presence of excess DDT while the nanoparticle samples with nearly identical optical signatures never result in the reformation of nanoclusters or dissolve on similar time scales, these data only support distinct crystalline structure from fcc gold.

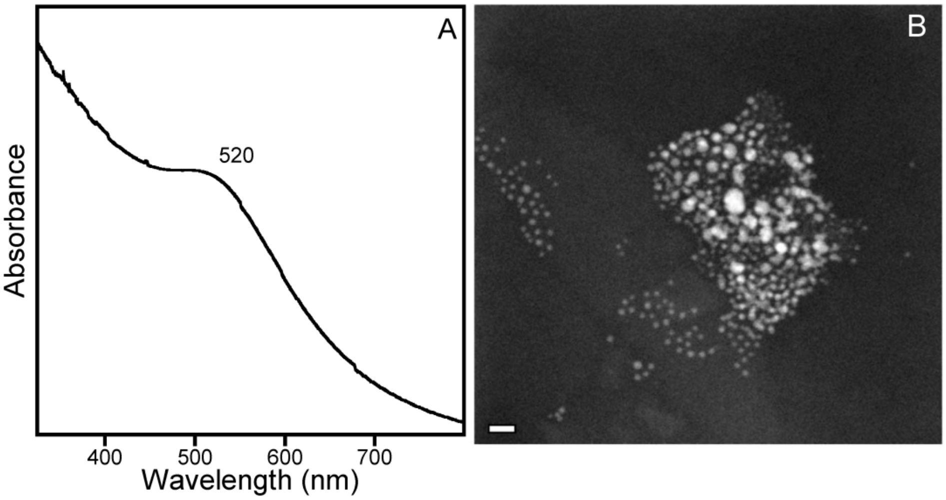

Figure S3. A) UV-Vis spectrum of DDT promoted dissolution of the film through equimolar addition of DDT to Au. The band centered at 520 nm is representative of gold species with diameters < 3 nm, which is consistent with observations for L^3 dissolution and intact films. B) STEM image representing a narrow distribution of dissolution products, where the scale bar represents 10 nm. Larger species result from incomplete destabilization of the film, but the individual nanocluster assemblies with diameters < 3 nm are clearly observed within the agglomerates.

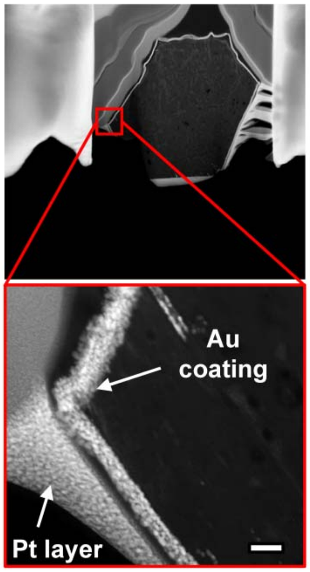

Figure S4. TEM image of cross-sectioned gold coated MIL-68(In) MOF. The FIB process likely alters the native structure of the deposited gold nanocluster assemblies. The scale bar in the inset represents 50 nm.

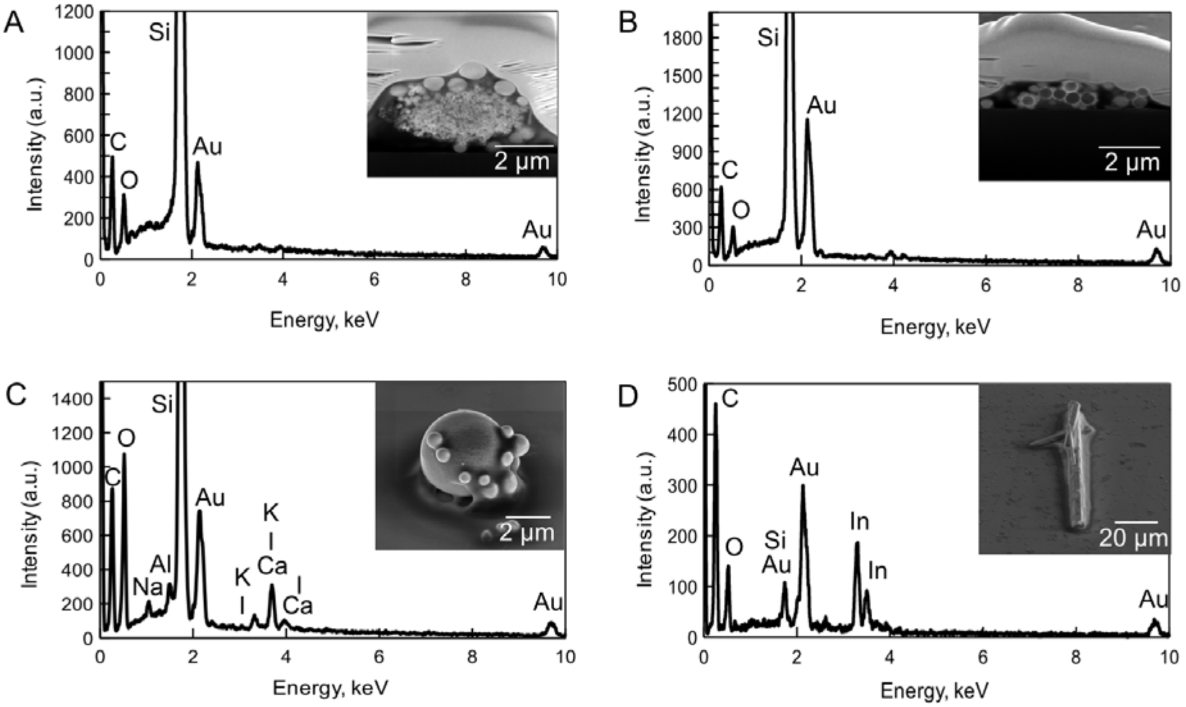

Figure S5. Energy dispersive X-ray spectra corresponding to structures shown in Figure 3 in main text: (A) Au coated 100 nm SiO_2 spheres, (B) Au coated 200 nm to 400 nm SiO_2 spheres, (C) Au coated 3.5 μm SiO_2 spherical shell, and (D) Au coated MIL-68(In) crystal.

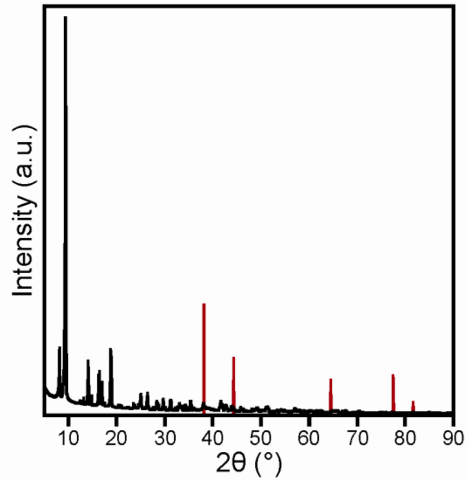

Figure S6. XRD pattern of Au coated MIL-68 crystal displaying no visible deterioration of the crystal structure after storage for 18 months. Red lines represent the fcc gold diffraction pattern.

MIL-68(In) FIB reconstruction: The reconstruction of the MIL-68(In) MOF structure presented through a series of FIB cross-sectioning and subsequent imaging steps. The presence of deposited gold (bright orange) on the exterior and interior surfaces is observed, which was achieved through the slow deposition process that is described in the experimental section. The native internal structure of the MOF crystal and gold is likely not preserved after FIB processing.

References and Notes:

1 Certain commercial materials and equipment are identified in this paper in order to adequately specify the experimental procedure. Such identification neither implies recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that the material or equipment identified is the best available for the purpose.

2 J. M. Pettibone; J. W. Hudgens. *ACS Nano* 2011**,** **5**, 2989.