Electron microscopy of gold nanoparticles at atomic resolution

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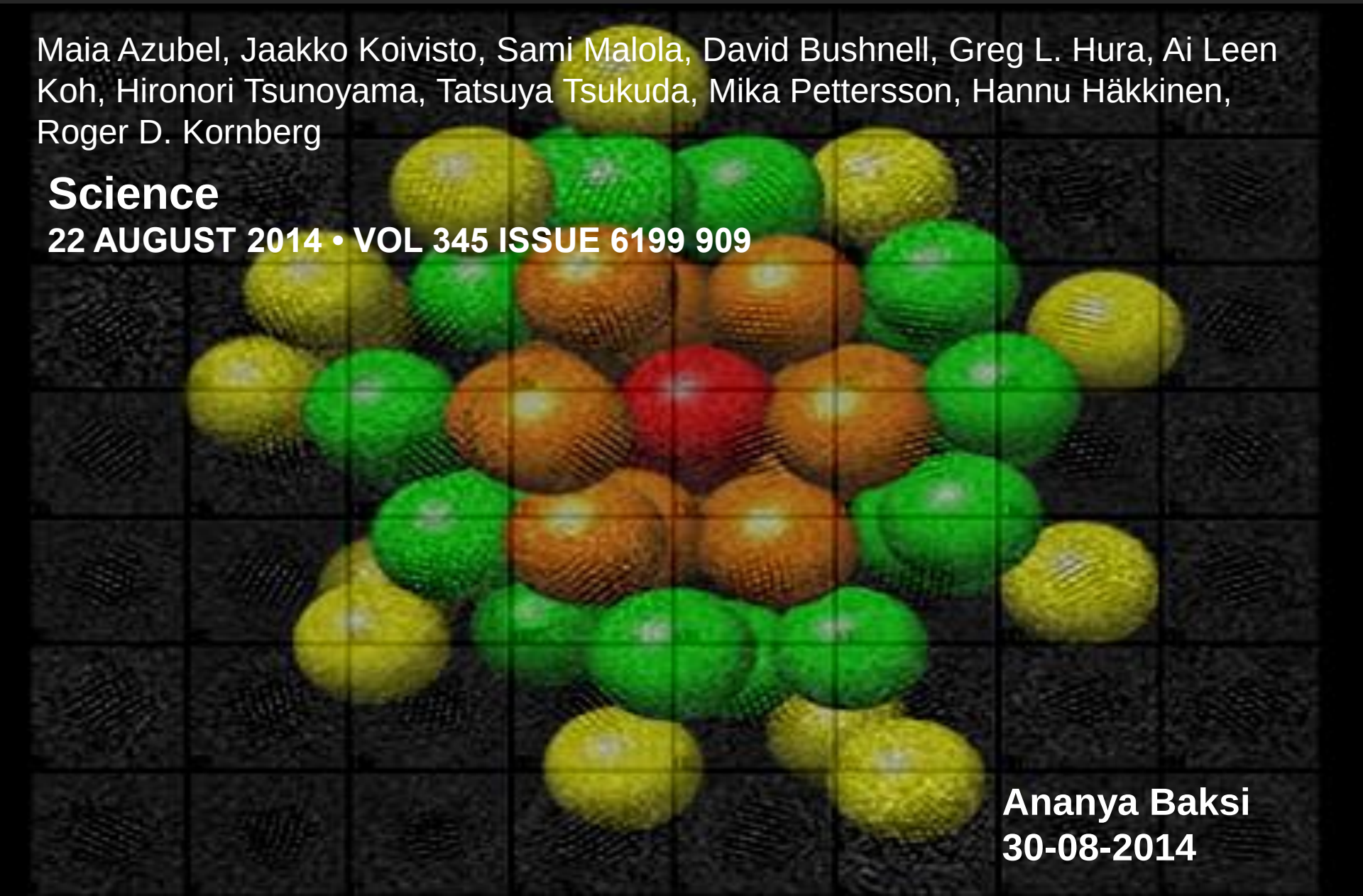

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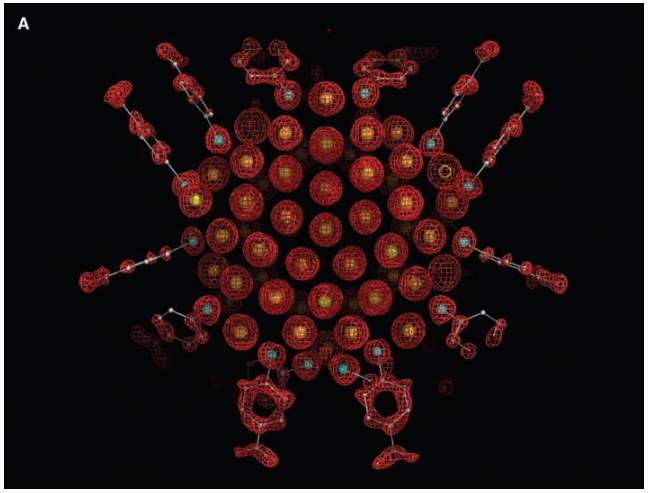
30-08-2014

Introduction

➢Particles on the order of 1 nm in diameter exhibit distinctive physical and chemical properties, with potential applications ranging from quantum electronics to biomedicine.

➢The x-ray crystal structure of a 102–gold atom NP ($Au_{102}NP$), 1.5 nm in diameter, showed the cluster of gold atoms surrounded by 44 thiolate ligands.



$Au_{102}(p\text{-}MBA)_{44}$

➢This atomic structure had threefold importance: (i) It identified the $Au_{102}NP$ as a molecule, with a precise composition and distinct arrangement of atoms; (ii) it led to the idea of the gold cluster as a “super atom,” stabilized by the filling of electron shells; and (iii) it revealed a layer of alternating gold and ligand molecules at the interface with solution.

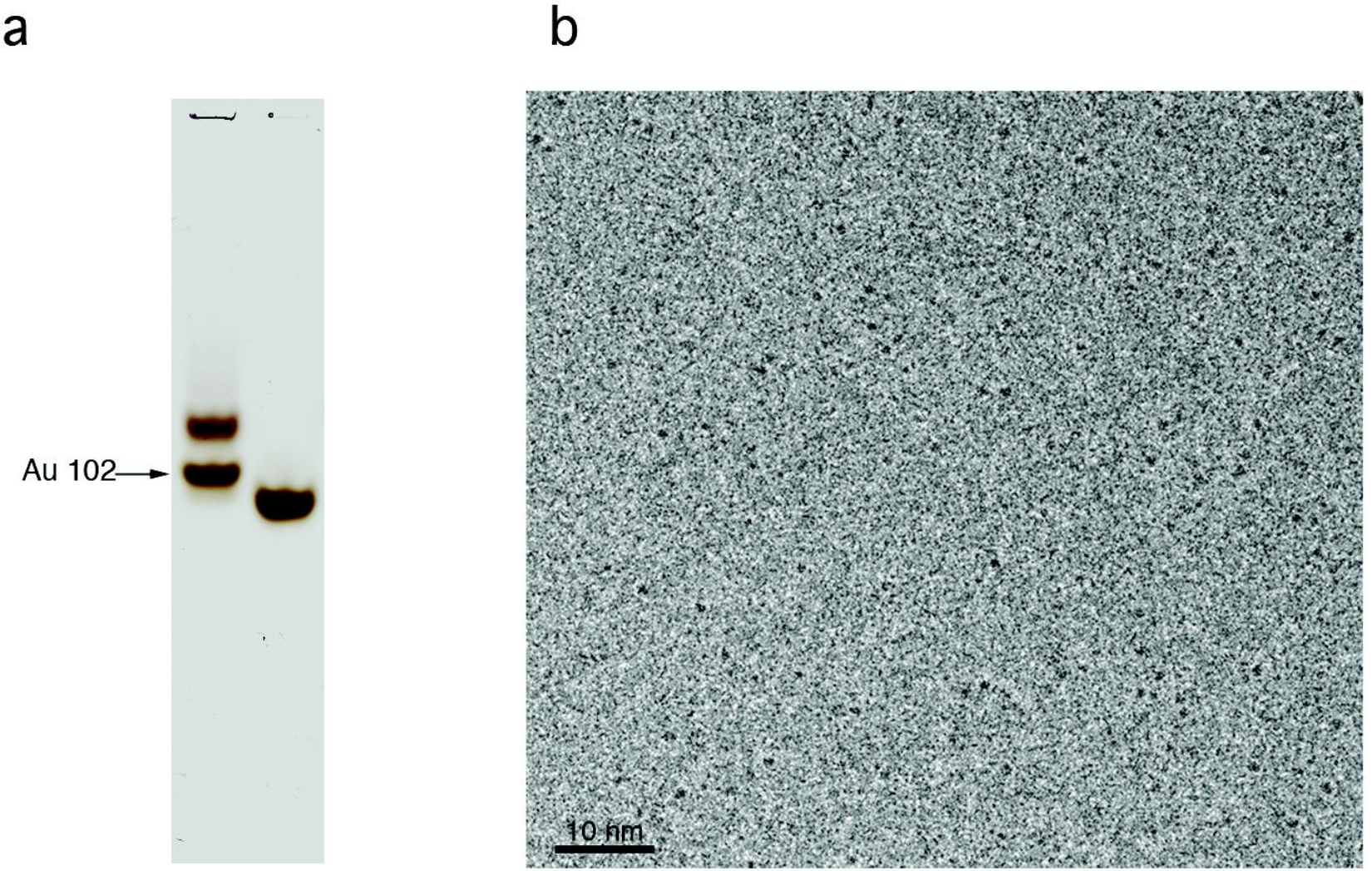
➢Although water-soluble AuNPs ranging from 1 to 3 nm in diameter have been crystallized, x-ray diffraction has not extended beyond ~5 Å resolution.

In this paper…

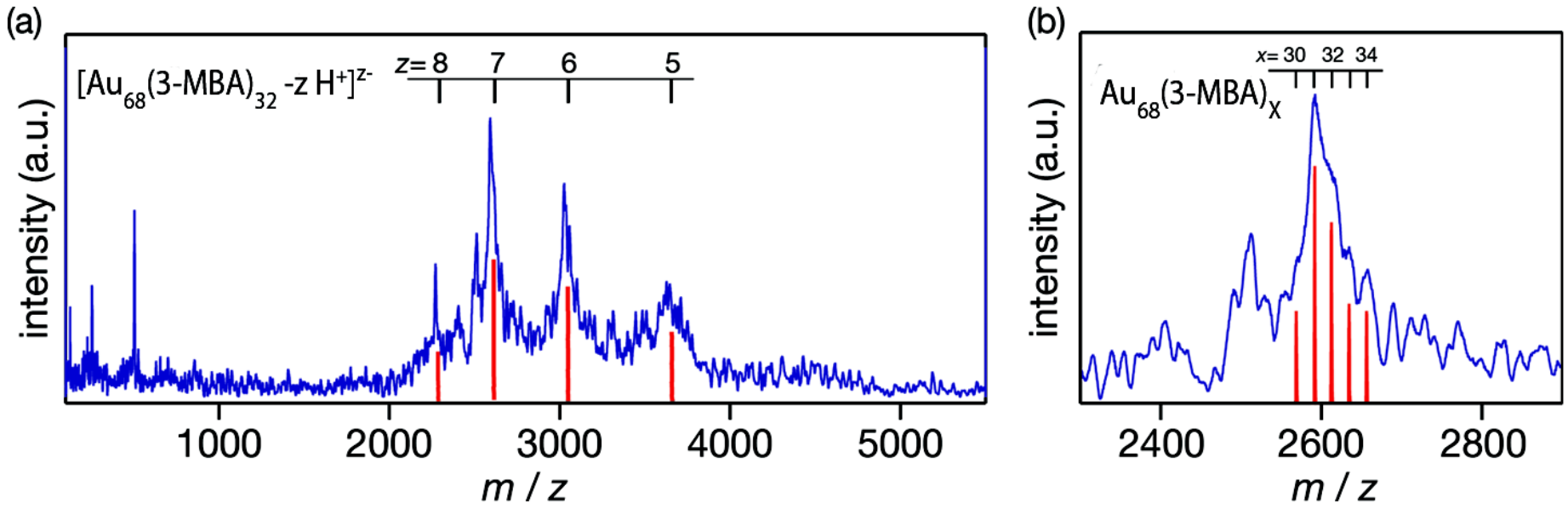
- The structure determination of a Au NP by a combination of a low-dose approach and aberration-corrected transmission electron microscopy (TEM), and they report an atomic structure with both similarities and notable differences from the Au_{102}NP.

- Whereas the thiolate ligand of the Au_{102}NP was p-mercaptobenzoic acid (p-MBA), they have now performed synthesis with 3-MBA, resulting in a different set of uniform, water-soluble particles.

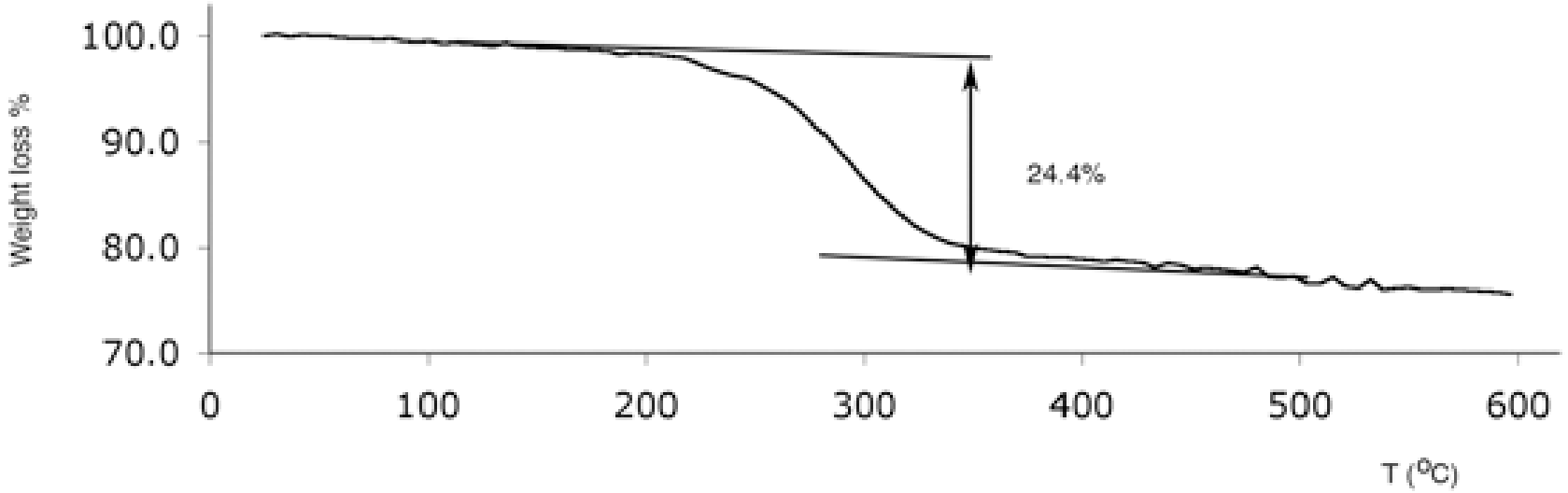
Results

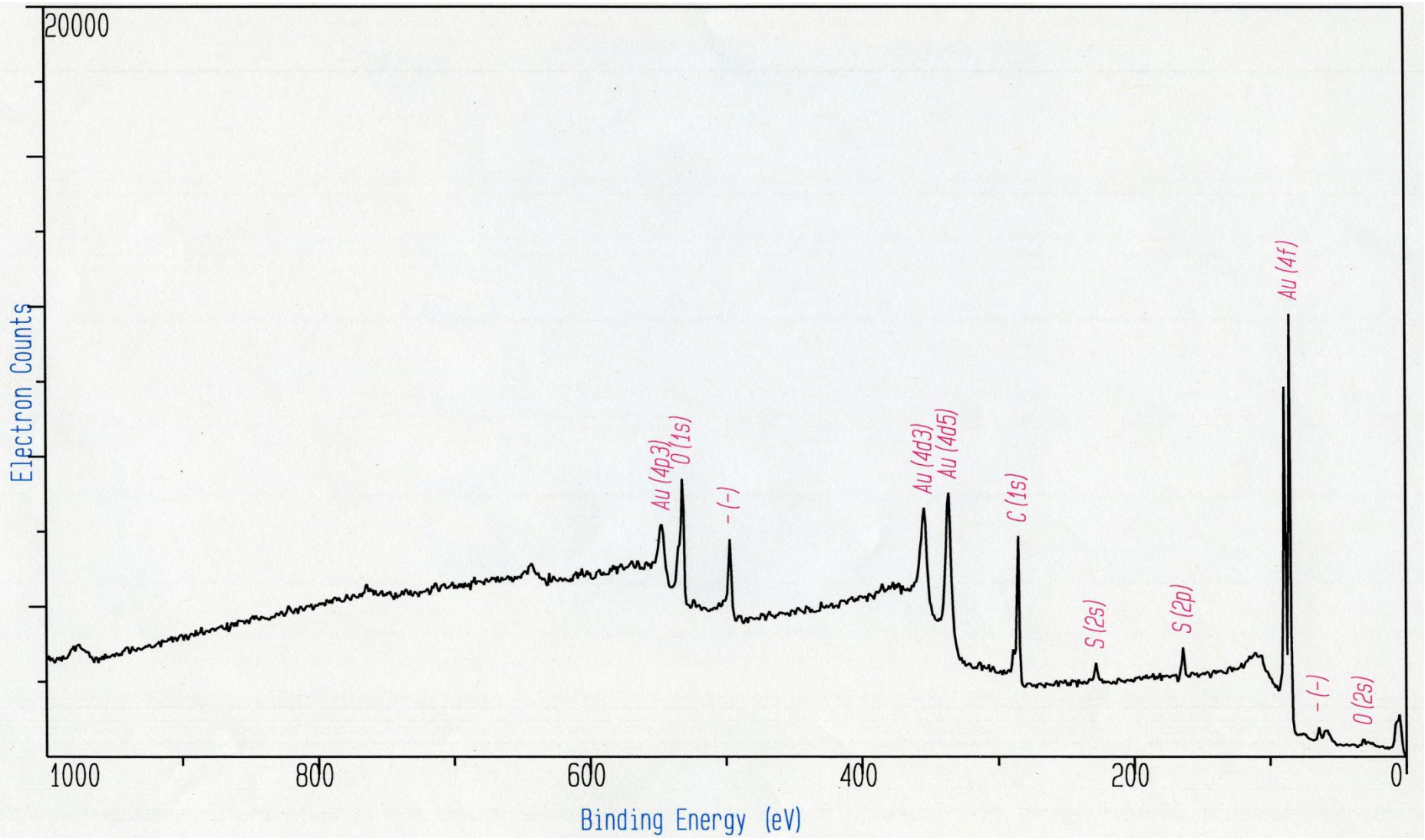


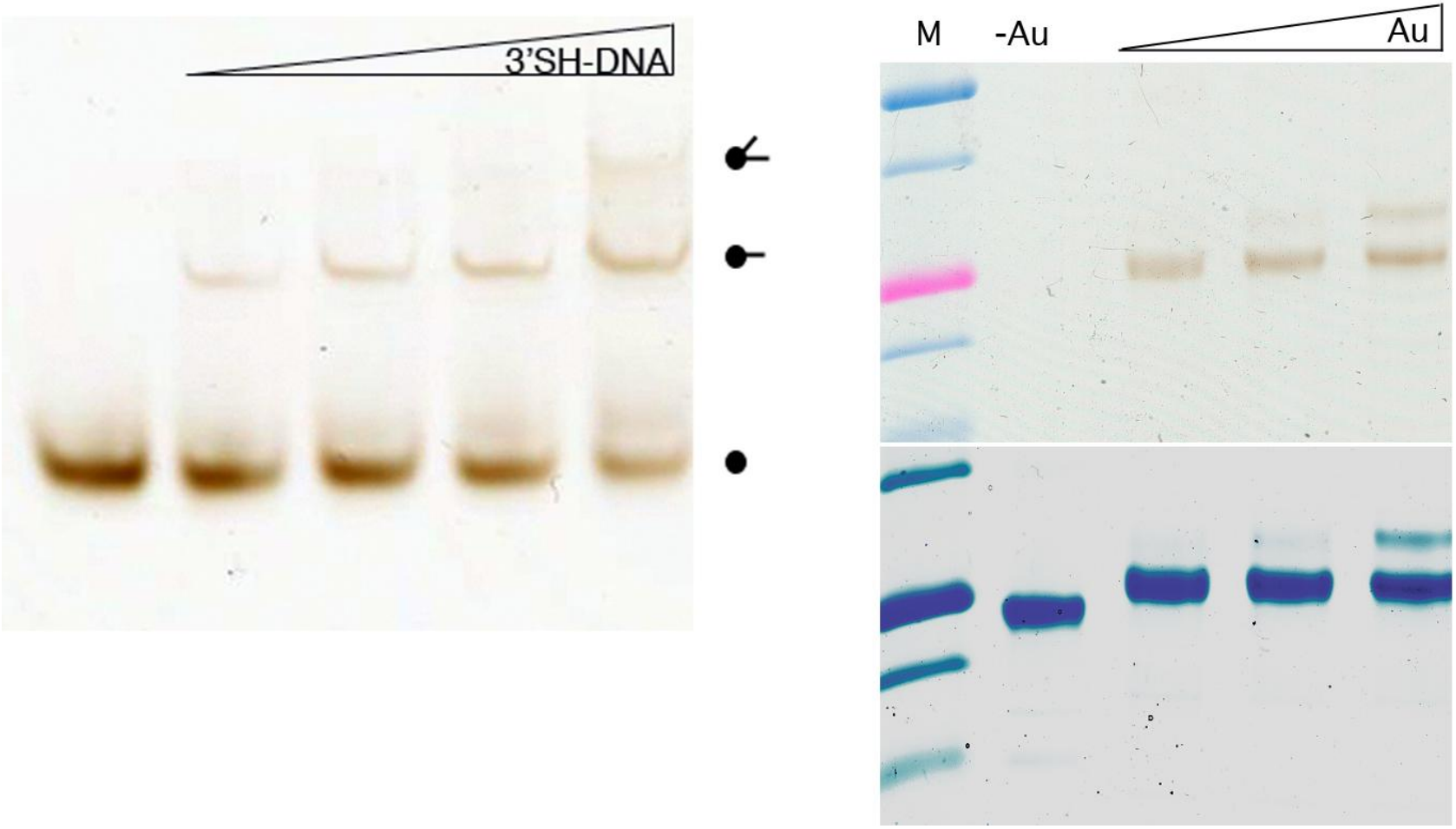
(a) Products obtained directly from $Au_{102}(p\text{-}MBA)_{44}$ (left lane) and Au_{68}NP (right lane) syntheses were run in a 12% PAGE. Arrow indicates $Au_{102}(p\text{-}MBA)_{44}$. (b) Cryo –EM micrograph of Au_{68} NP.



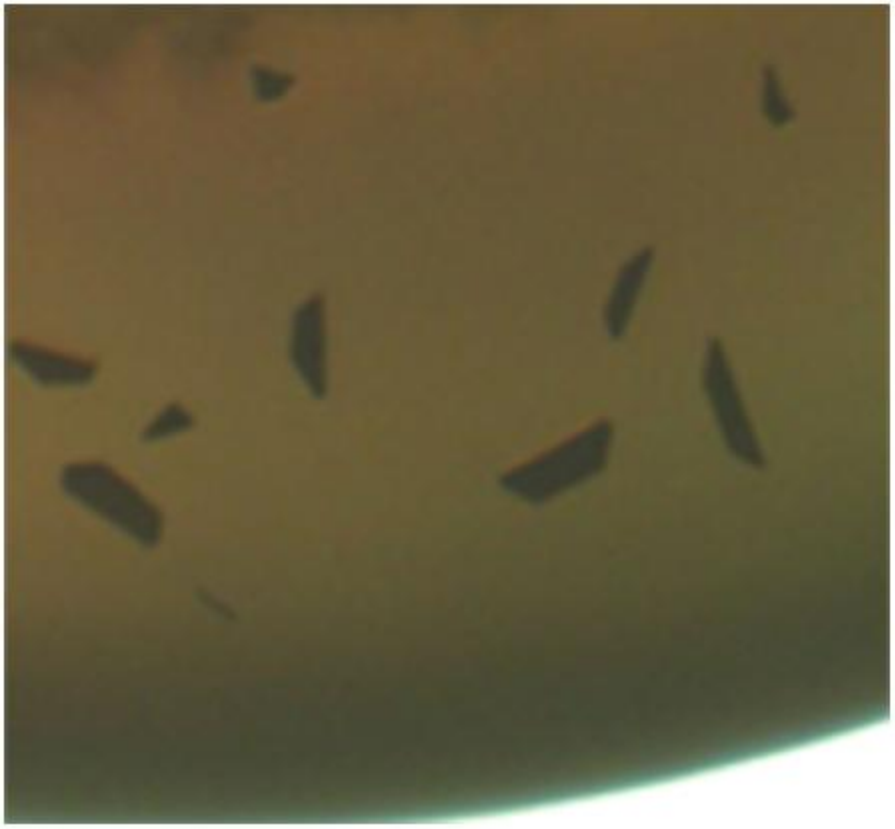
a) Full spectrum b) Close-up of 7- charge state peak.




20000
Electron Counts
Au (4p3)
O (1s)
- (-)
Au (4d3)
Au (4d5)
C (1s)
S (2s)
S (2p)
Au (4f)
- (-)
O (2s)
1000
800
600
400
200
0
Binding Energy (eV)

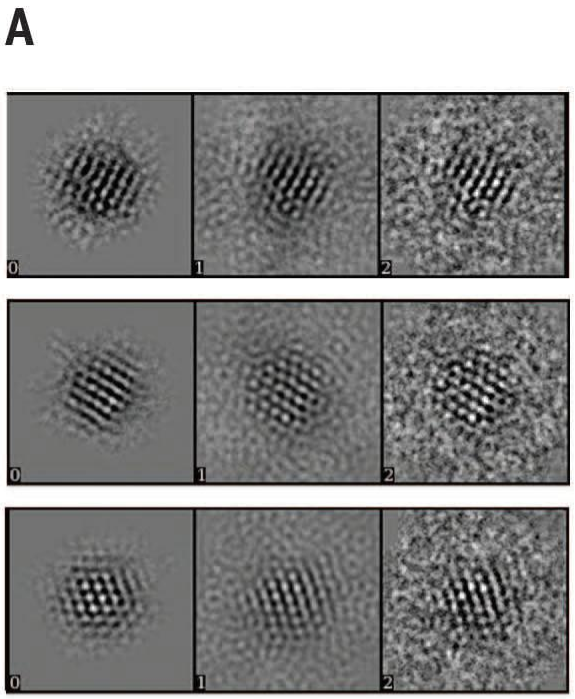


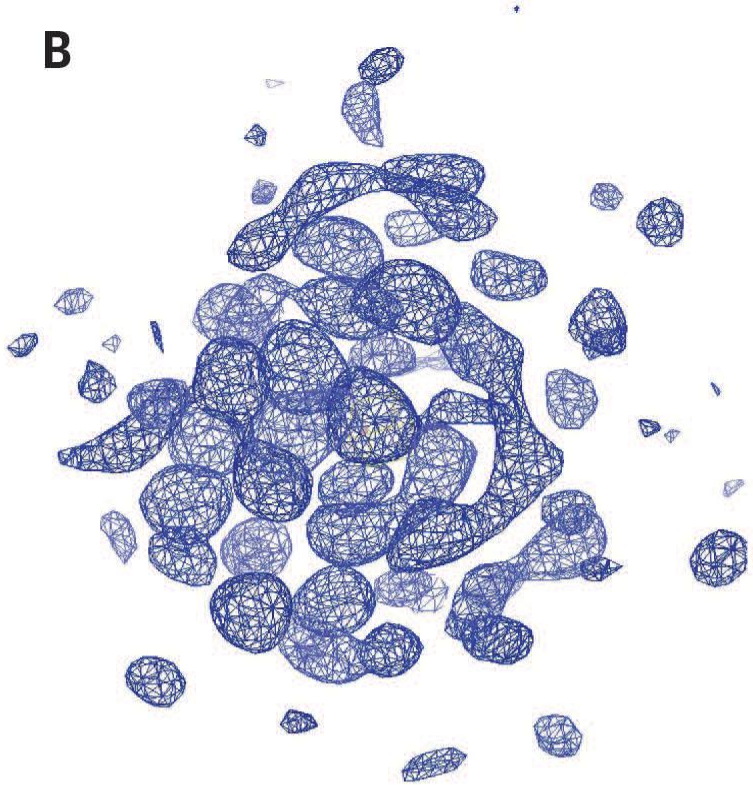
Bioconjugation of Au_{68}NP. (a) *Increasing concentration of 3'end thiol modified oligodeoxynucleotide (3'SH-DNA) incubated with Au68NP and analyzed by 12% PAGE. Diagram to the right: ball indicates free AuNPs ; ball with one or two bars indicate AuNPs conjugated to one or two, respectively, molecules of DNA. (b) Increasing concentration of Au_{68}NP incubated with scFv and analyzed by 10% SDS-PAGE, unstained (top panel) or stained with Coomassie blue (bottom panel). Left lane (M), precision plus protein standards (BioRad). Second lane from left (-Au), unlabeled scFv*

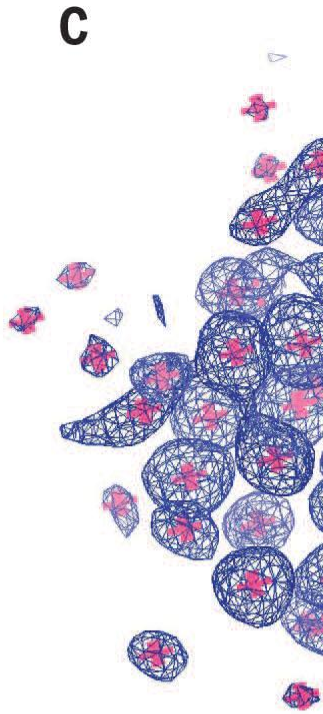


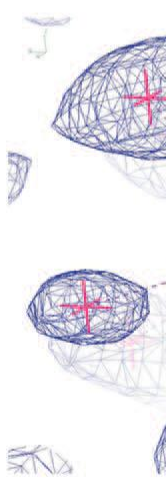
Crystals of Au_{68}NP imaged by light microscopy

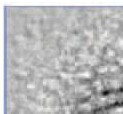
Crystals were grown by the hanging drop technique in a solution containing 50 mM magnesium acetate tetrahydrate and 20% w/v polyethylene glycol 3,350 at 16ºC.



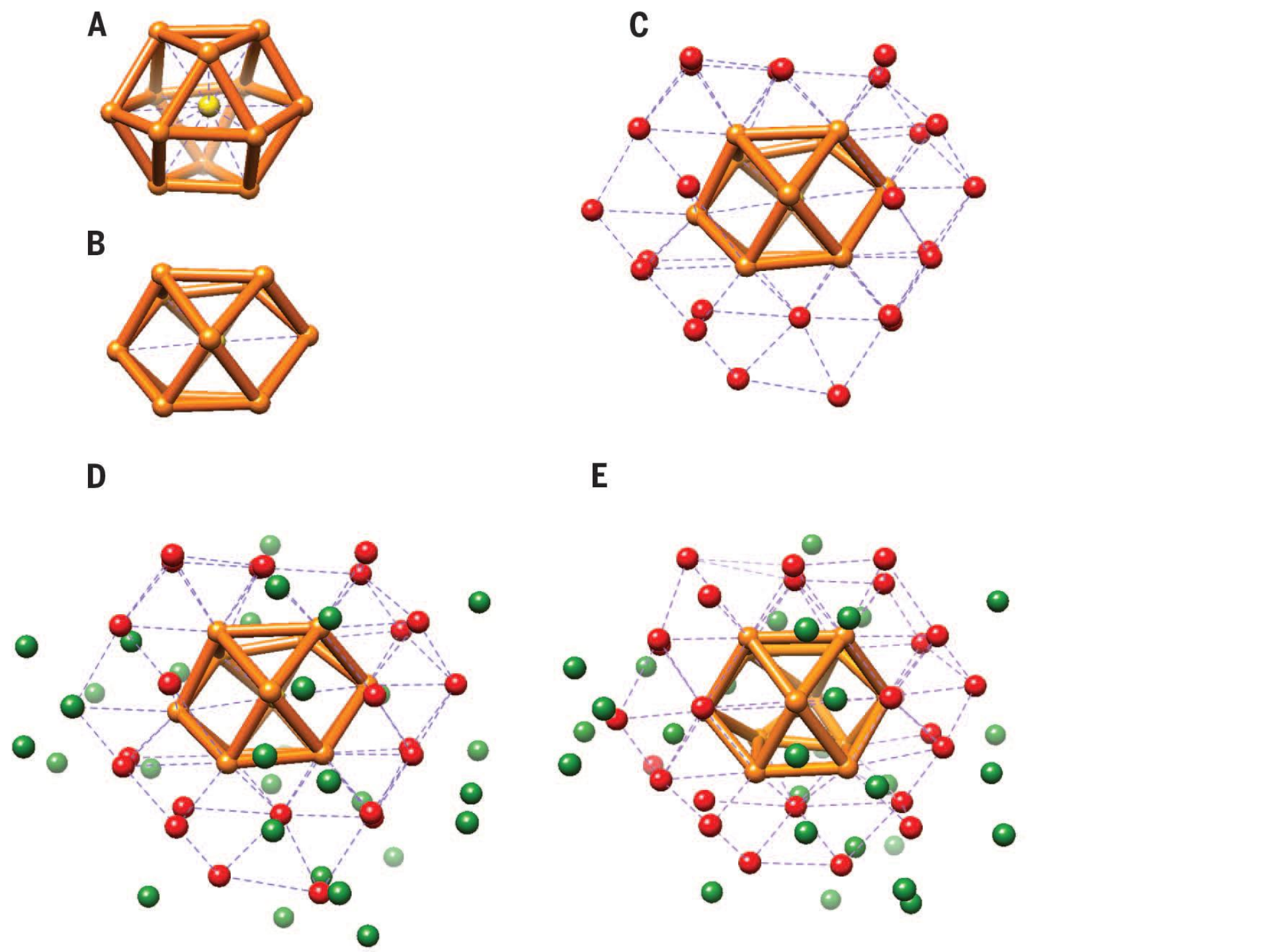


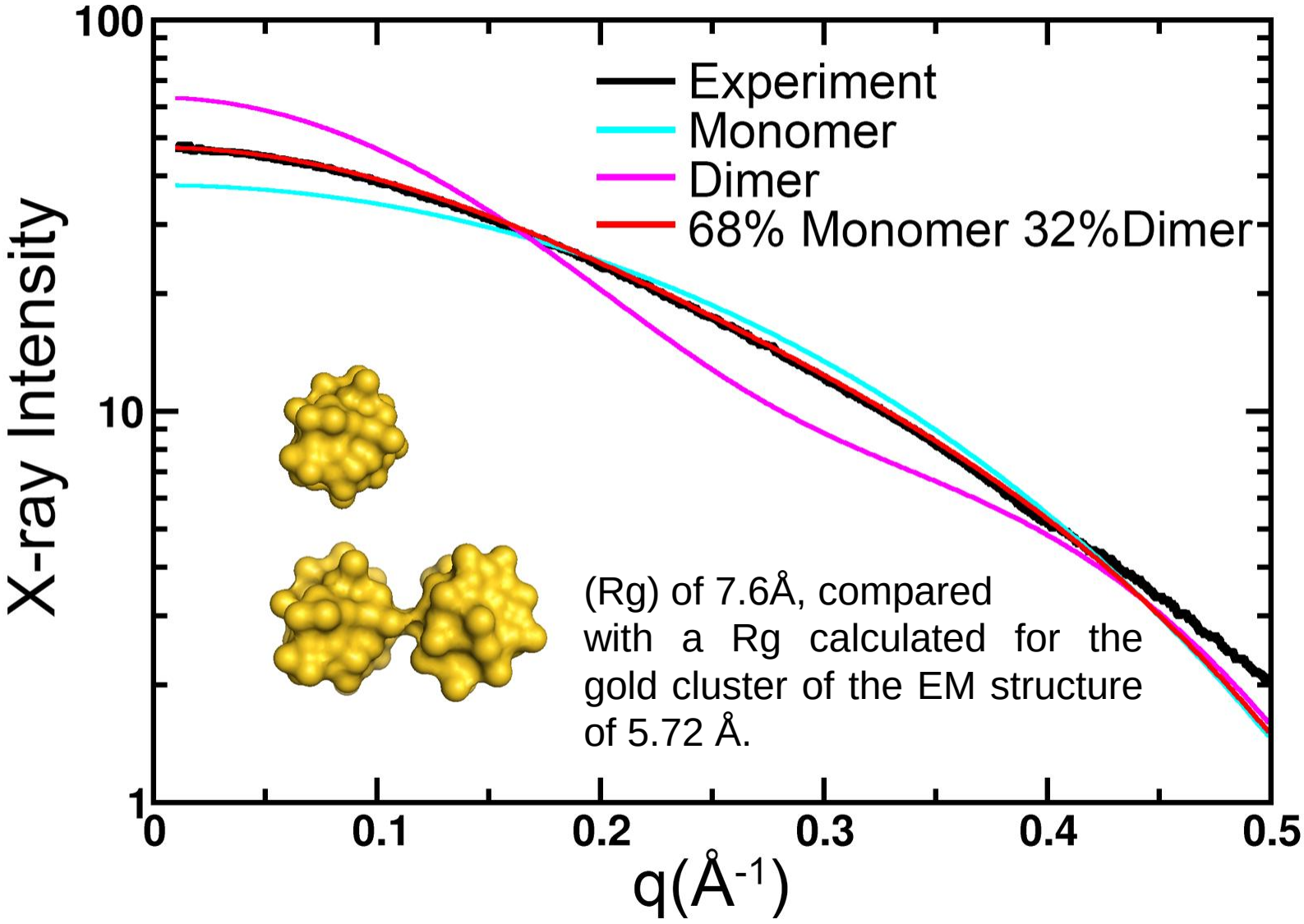




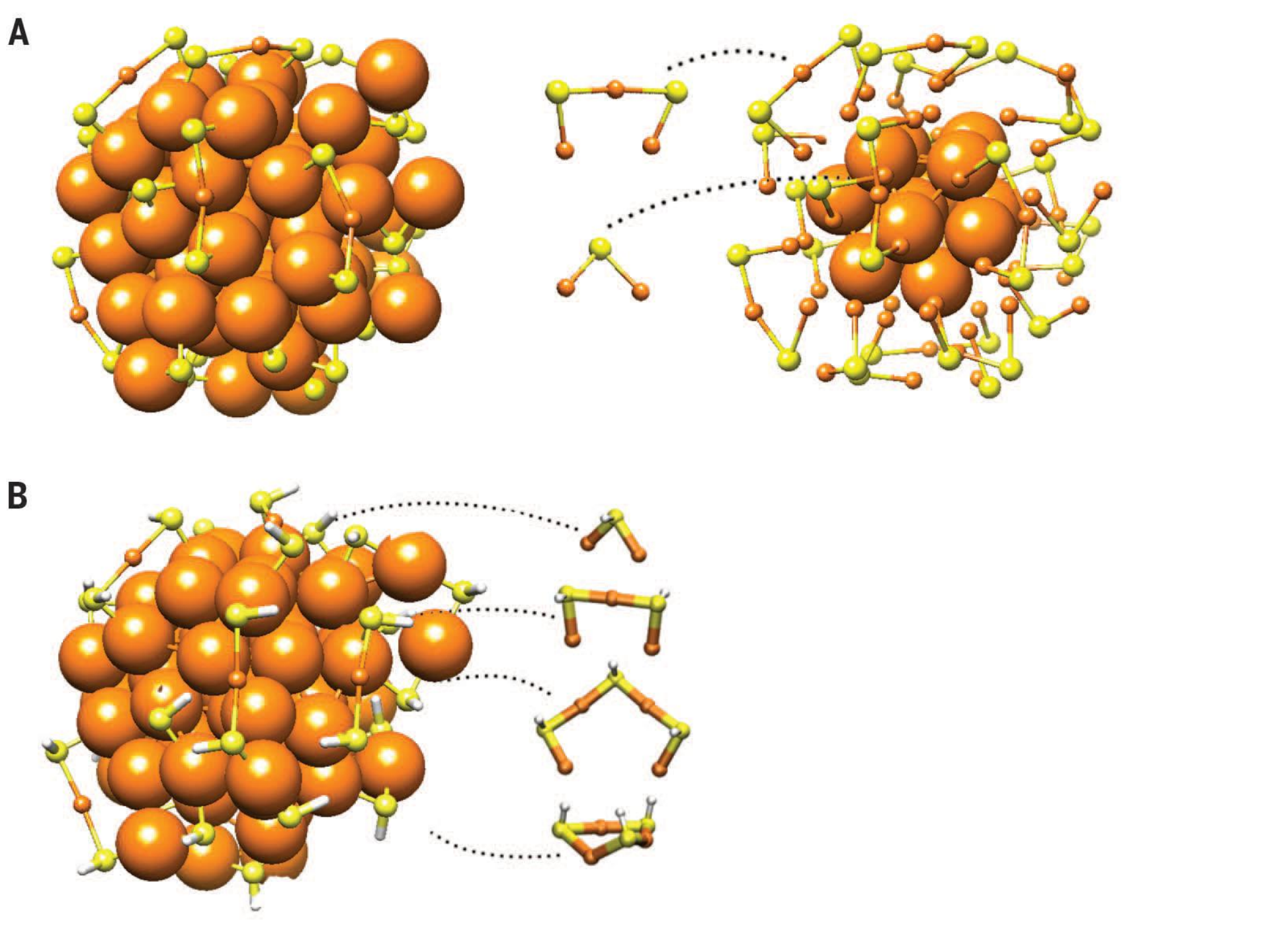


Three-dimensional (3D) reconstruction of Au_{68}NP structure from electron micrographs. (A) Representative components of the reconstruction. (Left) Back projection from the reconstruction; (middle) corresponding class average of the EM images; (right) EM images. (B to D) Electron density map, blue mesh. Pink stars in (C) and (D) show the position of atomic coordinates for gold atoms. (D) Region of the electron density map surrounding the central atom. Dashed lines show coordination of the central atom; numbers indicate gold-gold distances in angstroms. (E) A cross section of the 3D reconstruction (left) and its Fourier transform (right). The red arrow indicates spots at 2.4 Å resolution.

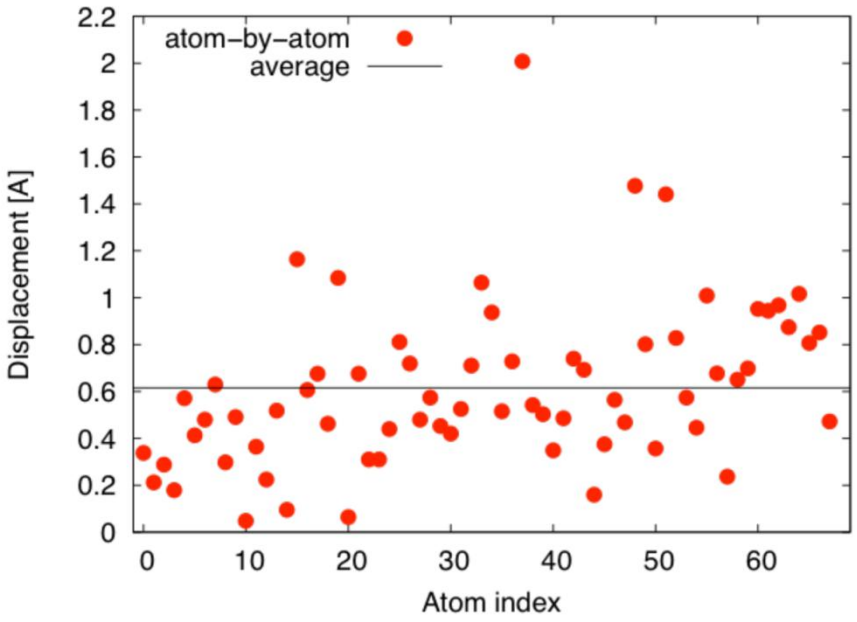

A
B
C
D
E



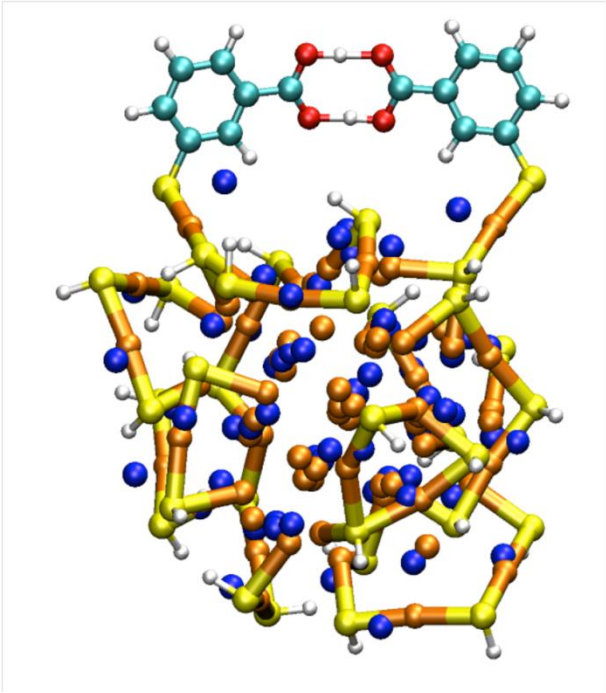
Small angle X-ray scattering (SAXS) from Au_{68}NPs. *Using atomic coordinates of monomers and modeled dimers (bottom inset) the calculated SAXS profiles were compared against experiment. A mixture (red) with a major population of monomer (cyan) and minor population dimer (magenta) had a best fit.*


A
B

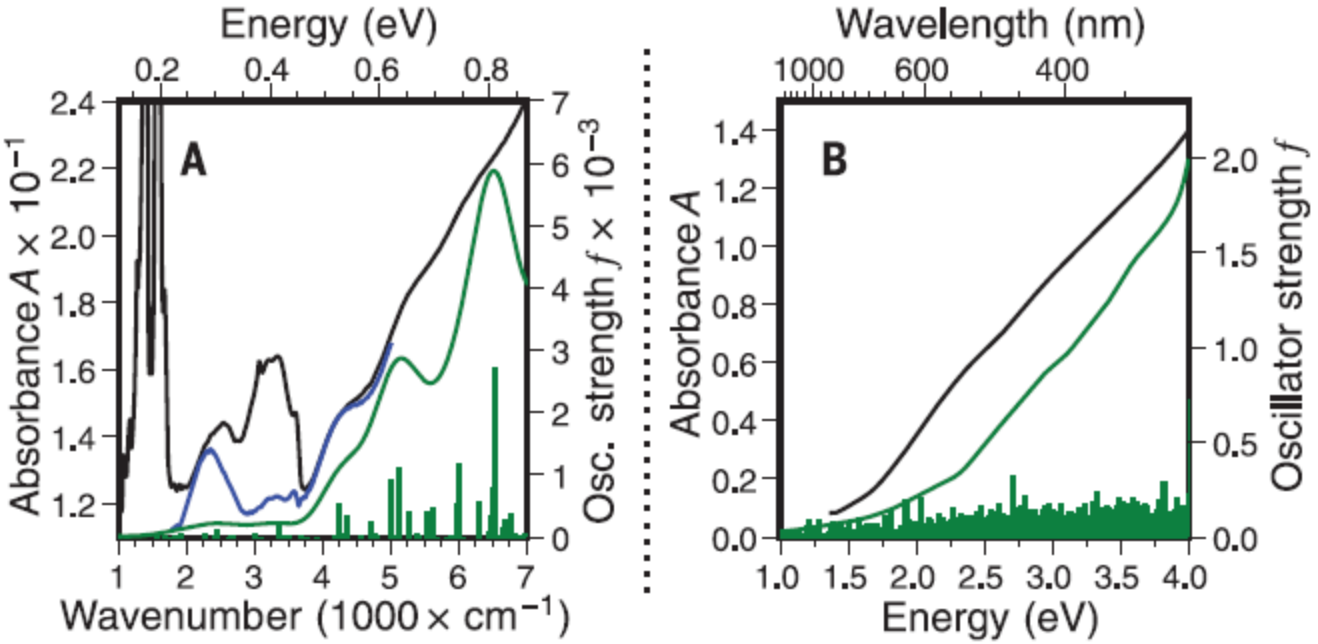
a



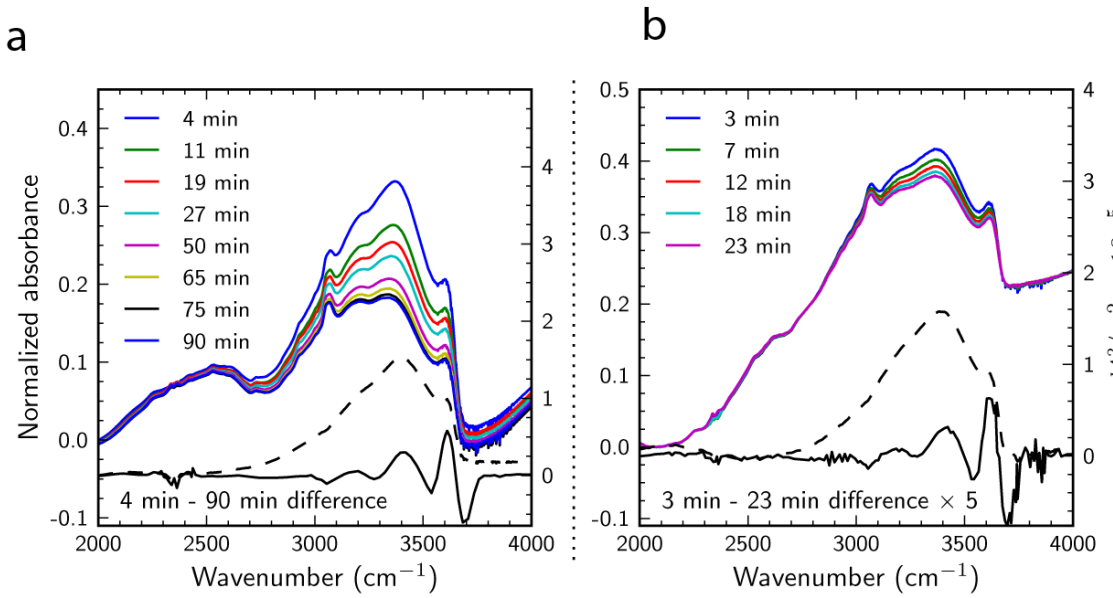
b

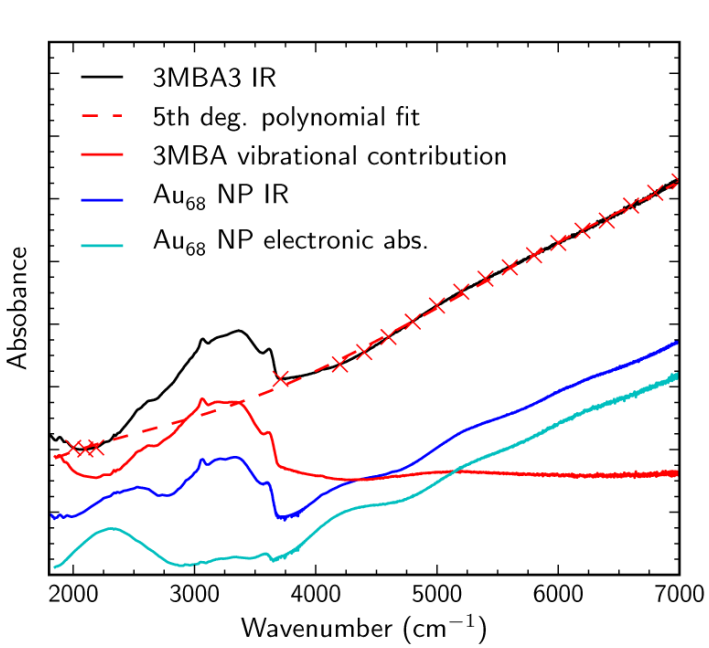


AC-TEM and DFT coordinators comparison *(a) Displacements of the gold atoms observed during the DFT relaxation of the* $Au_{68}(SH)_{32}$ *cluster, started from the experimental positions of gold in the EM data. (b) The DFT-relaxed model structure of* $Au_{68}(SH)_{30}(3\text{-MBA})_2$ *showing the special position of the Au-atoms in the double hydrogen bonded units including 3-MBA ligands. In the model structure sulfur atoms are represented in yellow, gold in orange, carbon in light blue, oxygen in red and hydrogen in white. The experimentally determined Au atom positions are shown in blue.*



Measured and computed absorption spectra of the Au_{68}NP. (A) IR region. (B) UV-vis region. Black curves, experimental data; green curves, LR-TDDFT-computed spectra obtained from the individual optical transitions (green vertical lines) with a Gaussian smoothing function [width 0.09 eV in (A) and 0.25 eV in (B)]. The blue curve in (A) denotes a spectrum from which the vibrational contribution has been subtracted by reference to a spectrum of a larger cluster with the same ligand layer (see fig. S10 for details). Both the computed and experimental data indicate that the lowest electronic transition occurs at 2500 cm−*1 (0.31 eV).*





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Summary and conclusion

- The notable findings of this work are: (i) the synthesis of a water-soluble AuNP, homogeneous in size, stable in solution, and nevertheless reactive toward sulfhydryl compounds, including proteins; (ii) the successful determination of atomic structure by EM, not previously reported; and (iii) the difference between the structure obtained and the only other structure of a large, water-soluble particle (the Au_{102}NP), solved by x-ray diffraction.
- Whereas the Au_{102}NP exhibits global symmetry (based on a truncated decahedral core), with all remaining atoms following fcc packing rules, the Au_{68}NP is based almost entirely on local fcc packing. The low-symmetry Au_{68}NP structure differs from a proposal from theory for a metal core of higher symmetry for an organosoluble particle of similar size, $Au_{67}(SR)_{35}$..
- Aberration-corrected transmission electron microscopes are capable of revealing individual heavy atoms.
- Implementation of low-dose techniques from biological TEM, combined with the power of the aberration-corrected transmission microscope, has revealed the atomic structure of a AuNP without any prior knowledge, model fitting, or assumptions about packing and should be generally applicable.

Thank You