

## Supporting information

# Chemically Selective Imaging of Individual Bonds Through Scanning Electron Energy-Loss Spectroscopy: Disulfide Bridges linking Gold Nanoclusters

*Karolina Sokolowska,<sup>\*†</sup> Zhongyue Luan,<sup>‡</sup> Eero Hulkko,<sup>†,§</sup> Christoph Rameshan,<sup>||</sup> Noelia*

*Barrabés,<sup>||</sup> Vartkess A. Apkarian,<sup>⊥</sup> Tanja Lahtinen<sup>\*†</sup>*

<sup>†</sup>Department of Chemistry, Nanoscience Center, University of Jyväskylä, P.O. Box 35,  
40014 Jyväskylä, Finland.

<sup>‡</sup>Department of Material Science and Engineering, University of California, Irvine, Irvine,  
CA 92697, USA.

<sup>§</sup>Department of Electronics and Nanoengineering, Aalto University, P.O. BOX 11000, FI-  
00076, Finland.

<sup>||</sup>Faculty of Technical Chemistry, Institute of Materials Chemistry, Technische Universität  
Wien, 1060 Vienna, Austria.

<sup>⊥</sup>Department of Chemistry, University of California, Irvine, Irvine, CA 92697, USA.

### Corresponding Authors

Email: *karolina.x.sokolowska@jyu.fi*; *tanja.m.lahtinen@jyu.fi*

## Experimental section

### 1. Materials

The covalently linked chains of Au<sub>230</sub>(pMBA)<sub>~80</sub> clusters (Au<sub>230</sub>) were prepared according to previously published synthesis procedure using 5,5'-bis(mercaptomethyl)-2,2'-bipyridine (BMM-BPy) as the bridging molecule.<sup>1,2</sup> All reagents were commercially available. The synthesis initially yielded a distribution of various sizes of oligomers. The trimer fraction, formed by three atomically precise gold clusters, was separated by polyacrylamide gel electrophoresis (PAGE). The as-prepared linked clusters were characterized prior to the measurements by TEM and UV-vis spectroscopy.

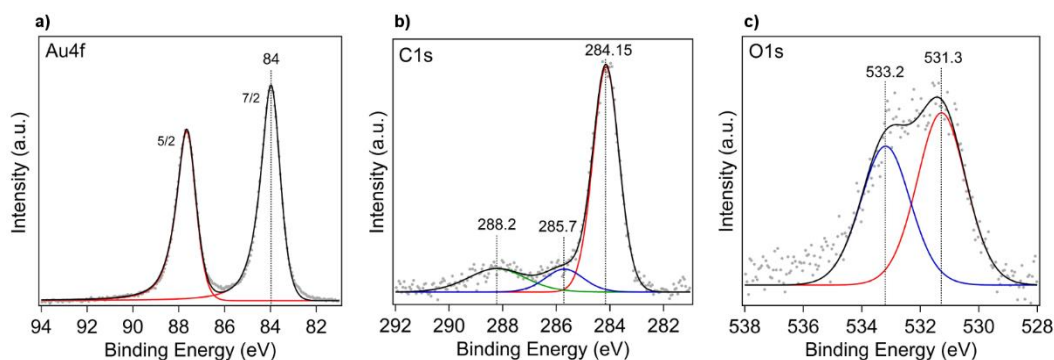
### 2. Microscopic characterization

Particle size, morphology, and composition were characterized by using STEM. The sample was prepared by dispersing eight microliters of aqueous solution (ddH<sub>2</sub>O) of covalently linked gold trimers onto a glow discharged graphene copper grid for a few minutes and blotted from the side to remove excess liquid. The grid was submerged in methanol, water, and methanol, sequentially and dried. Due to the reported difficulty of direct imaging of small (~2 nm) metal particles using conventional electron microscopy, a double aberration-corrected STEM JEOL-JEM300CF was used to obtain structural information. The STEM imaging was performed at 80 keV with STEM 0.1 nm resolution. The Gatan TEM Analytical Holders and Gatan detector were used. All sample holders were cleaned by O<sub>2</sub>/Ar plasma in the Advanced Plasma System (Gatan, Model 950) to remove hydrocarbon contaminants before loading the sample grid. To identify the composition and distribution of the gold structures, STEM imaging and EELS were carried out on the sample on JEM-ARM300F at 80 keV with Gatan TEM Analytical Holders using Gatan GIF Quantum detector. Spectrum fitting and mapping were performed using Gatan Microscopy Suite® (GMS) software.

### 3. X-ray Photoelectron spectroscopy

For the XPS measurements, the dry sample was applied evenly on carbon tape. Measurements were performed on a lab-based *in situ* NAP-XPS system equipped with a Phoibos 150 NAP hemispherical analyzer and an XR 50 MF X-ray source (microfocus), all SPECS GmbH. Spectra were recorded with monochromatic Al K $\alpha$  radiation and data were analyzed with the CasaXPS software. The XPS peaks were fitted after Shirley for Au 4*f* and linear background subtraction for S 2*p* with Gauss–Lorentz sum functions. For the Au 4*f* signals, an asymmetric line shape was applied. Peak positions and full width at half-maximum (FWHM) were left unconstrained. Au 4*f* peaks were fitted with 3.7 eV doublet separation and a fixed ratio of 4:3 for Au 4*f* 7/2 and Au 4*f* 5/2. For the S 2*p* peak, doublets with a fixed separation of 1.2 eV and a fixed area ratio of 2:1 were used for S 2*p* 3/2 and S 2*p* 1/2 (all NIST XPS database). Peak positions were referenced to the valence band signal (fermi edge).

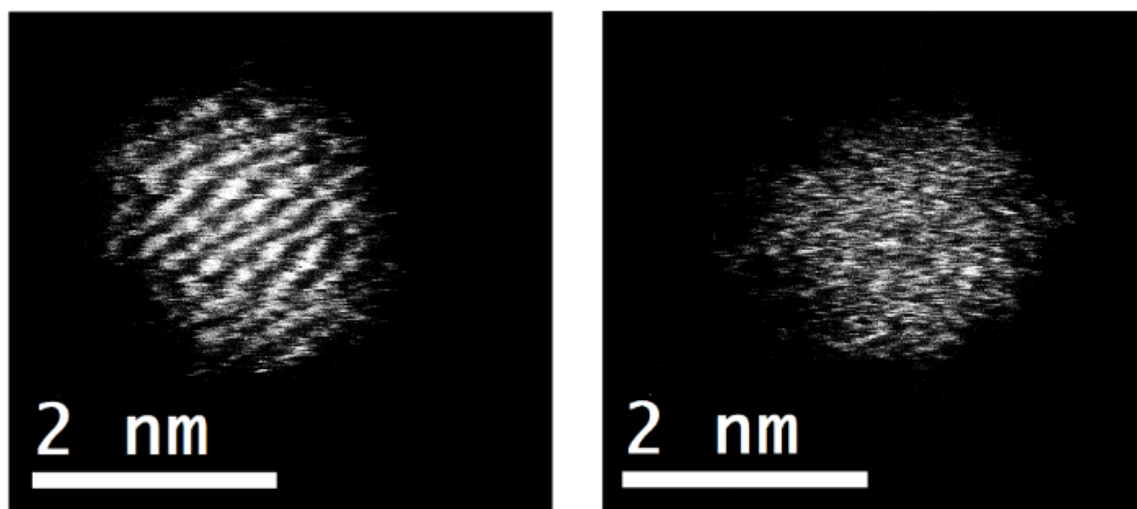
#### Supplementary figures



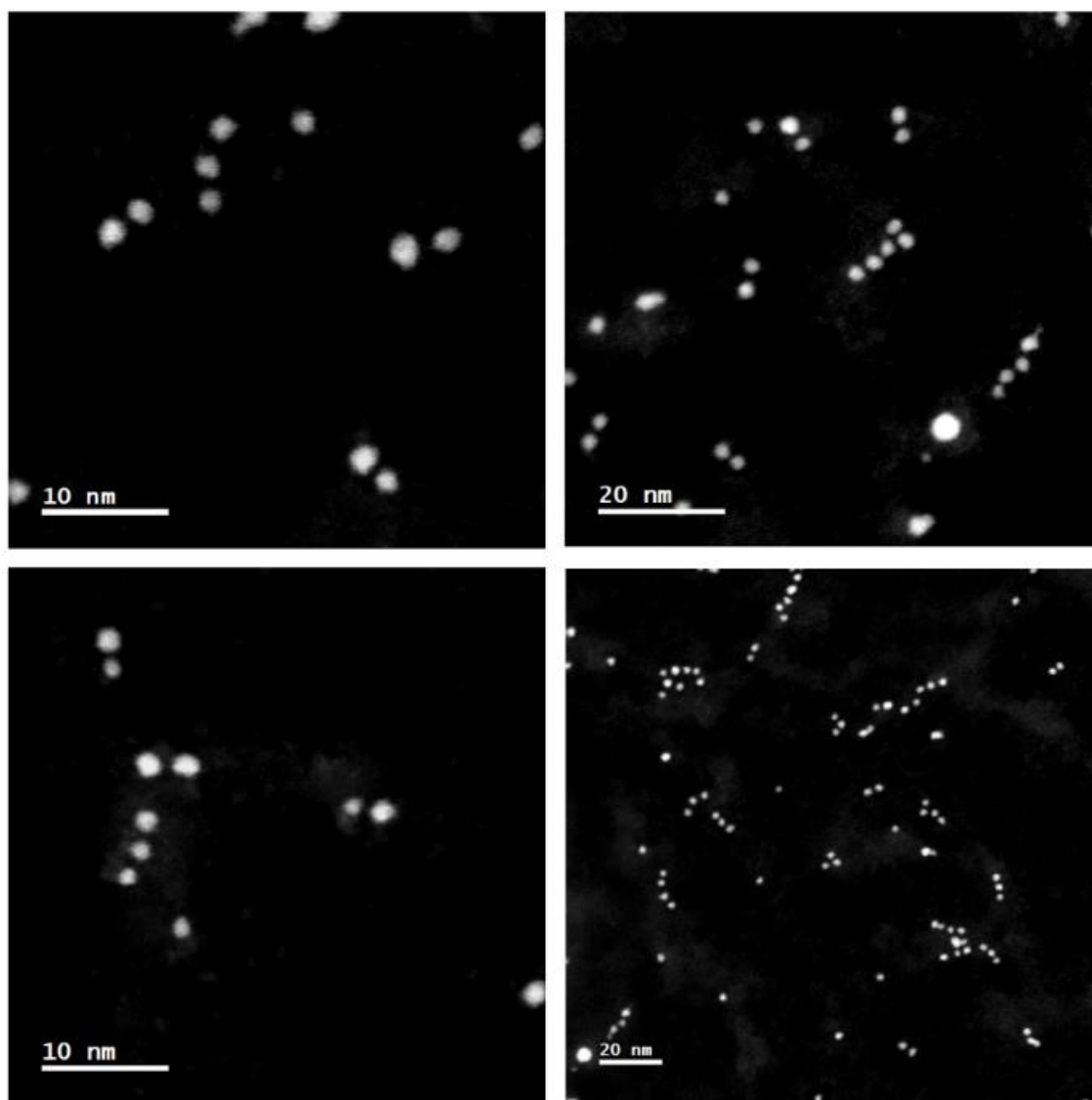
**Figure S1.** XPS (a) Gold 4*f* spectrum of linked oligomers; the signal is fitted with doublets for 4*f* 7/2 and 4*f* 5/2. Note the peak at 84 eV with an asymmetric line shape similar to that observed for bulk gold (b) Carbon 1*s* spectrum; The component at ~284.2 is attributed to C from the aromatic ring and (c) Oxygen 1*s* spectrum; trace amounts of oxygen were observable in the sample.

**Table S1.** Binding energy, FWHM values and identified species from Au superstructures sample.

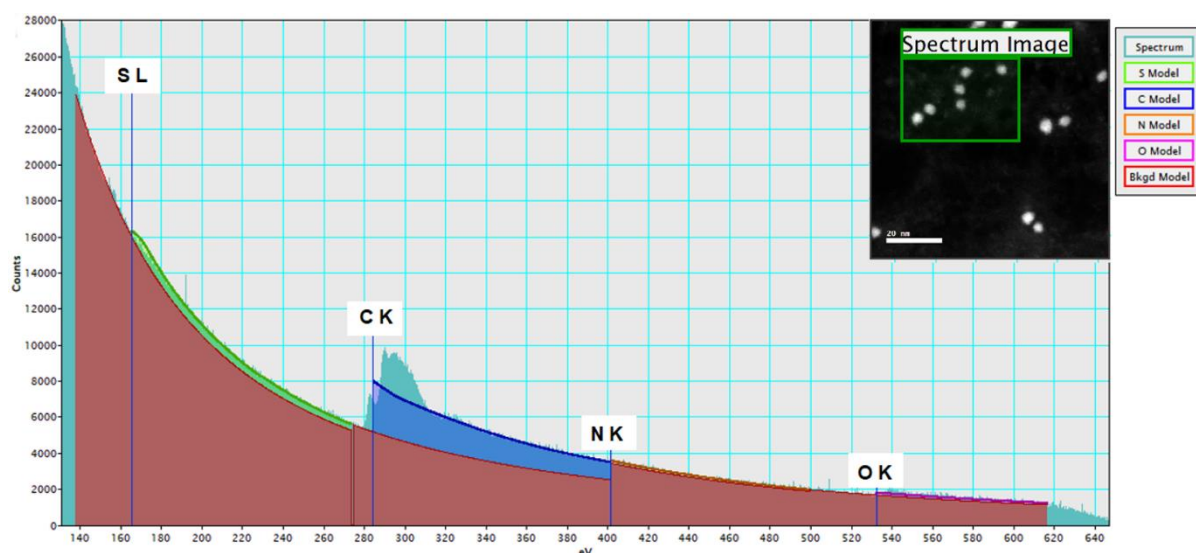
| Element | Binding energy/eV | FWHM/eV | Species/assigned as |
|---------|-------------------|---------|---------------------|
| Au 4f   | 84                | 0.95    | Au                  |
| S 2p    | ~162.5            | ~1      | Au-S-R              |
|         | 164.6             | ~1.5    | R-S-S-R             |
| S 2s    | 226.7             | ~2      | Au-S-R              |
|         | 228.5             | ~2      | R-S-S-R             |
| C 1s    | ~284.2            | 1.15    | Carbon              |
| O 1s    | ~531.3            | 1.95    | Oxygen              |



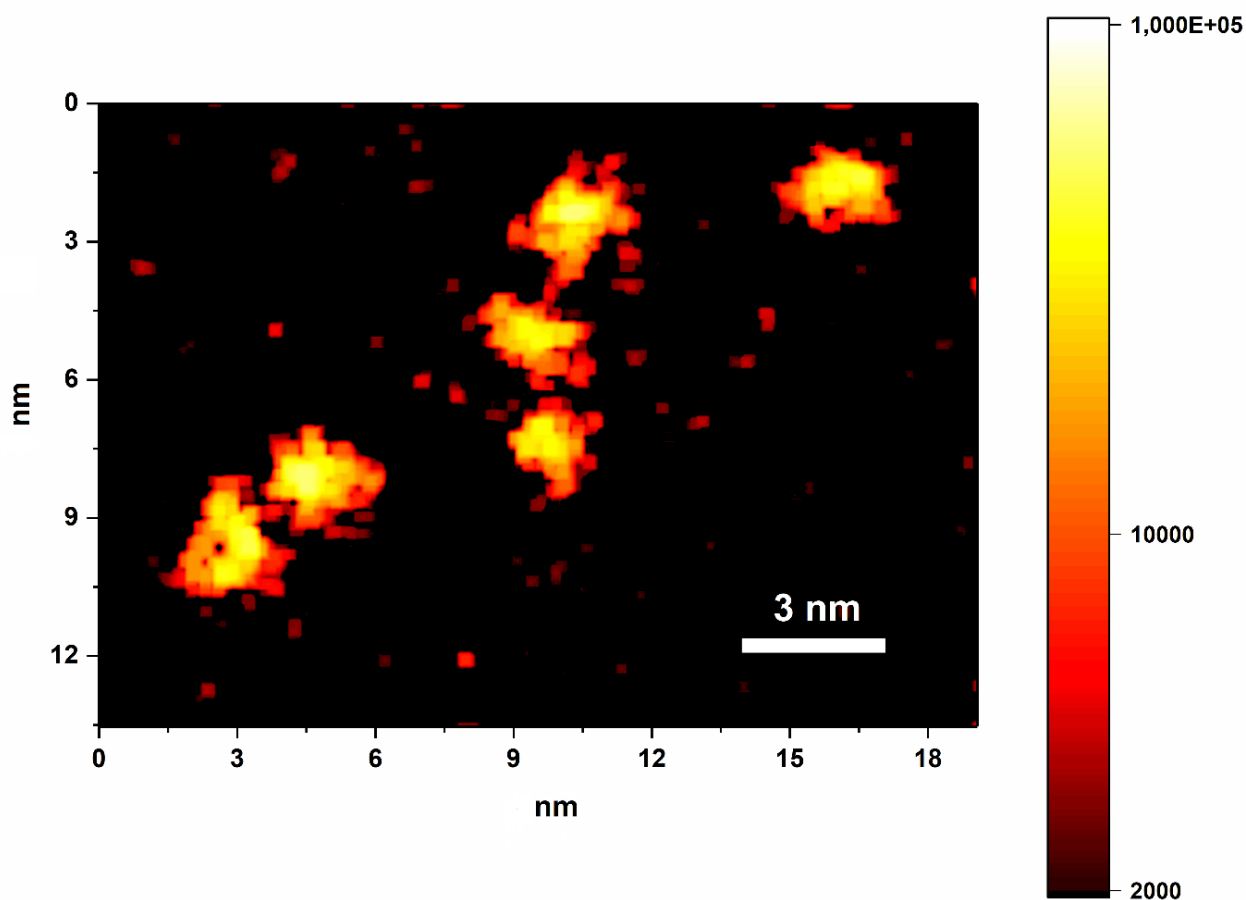
**Figure S2.** STEM micrographs of a single  $\text{Au}_{210-230}(\text{pMBA})_{70-80}$  cluster. The discontinued strips on the left image are due to sample drifting.



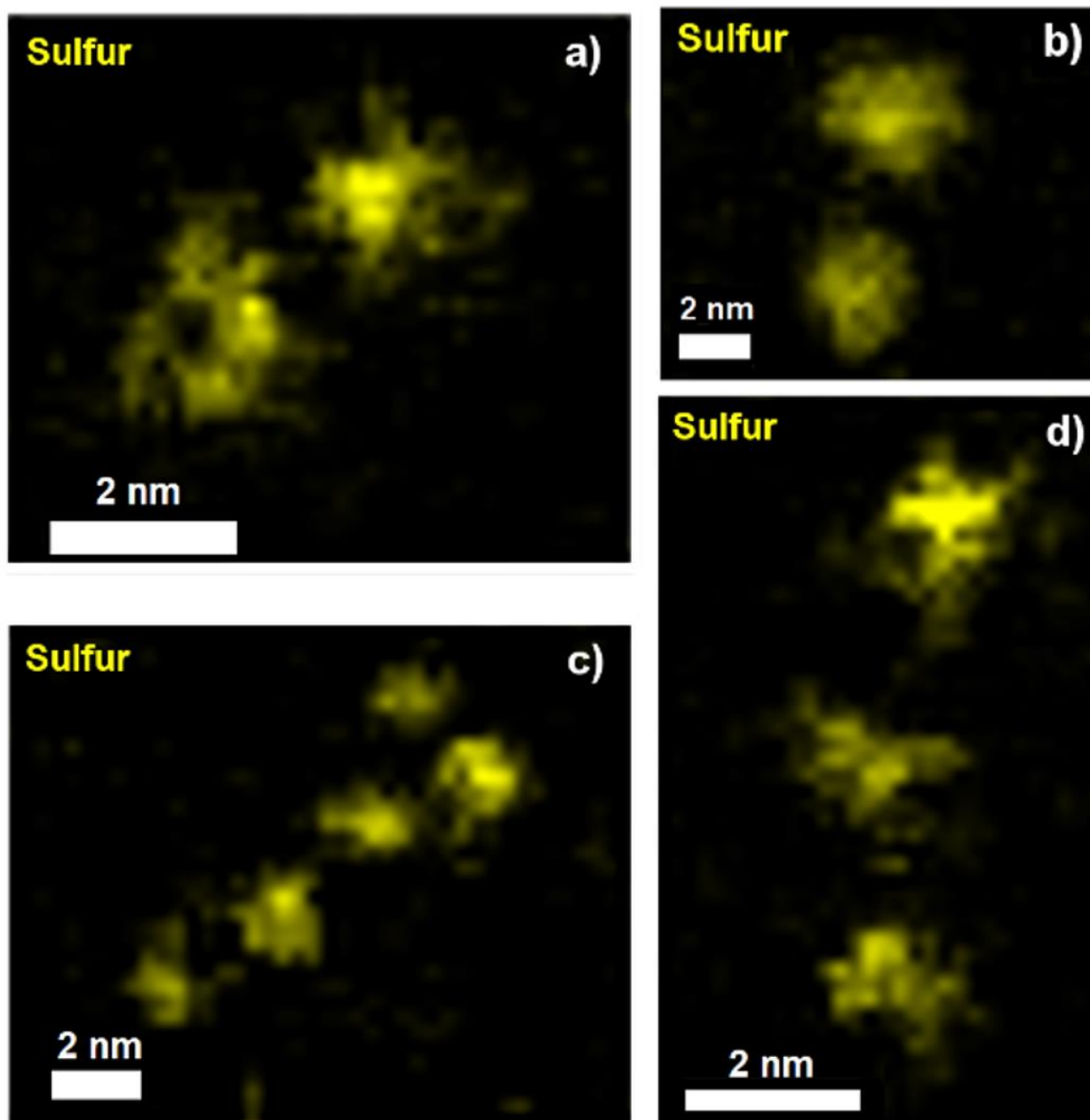
**Figure S3.** STEM micrographs of covalently-linked Au<sub>230</sub> trimers using BMM-BPy as the bridging molecule.



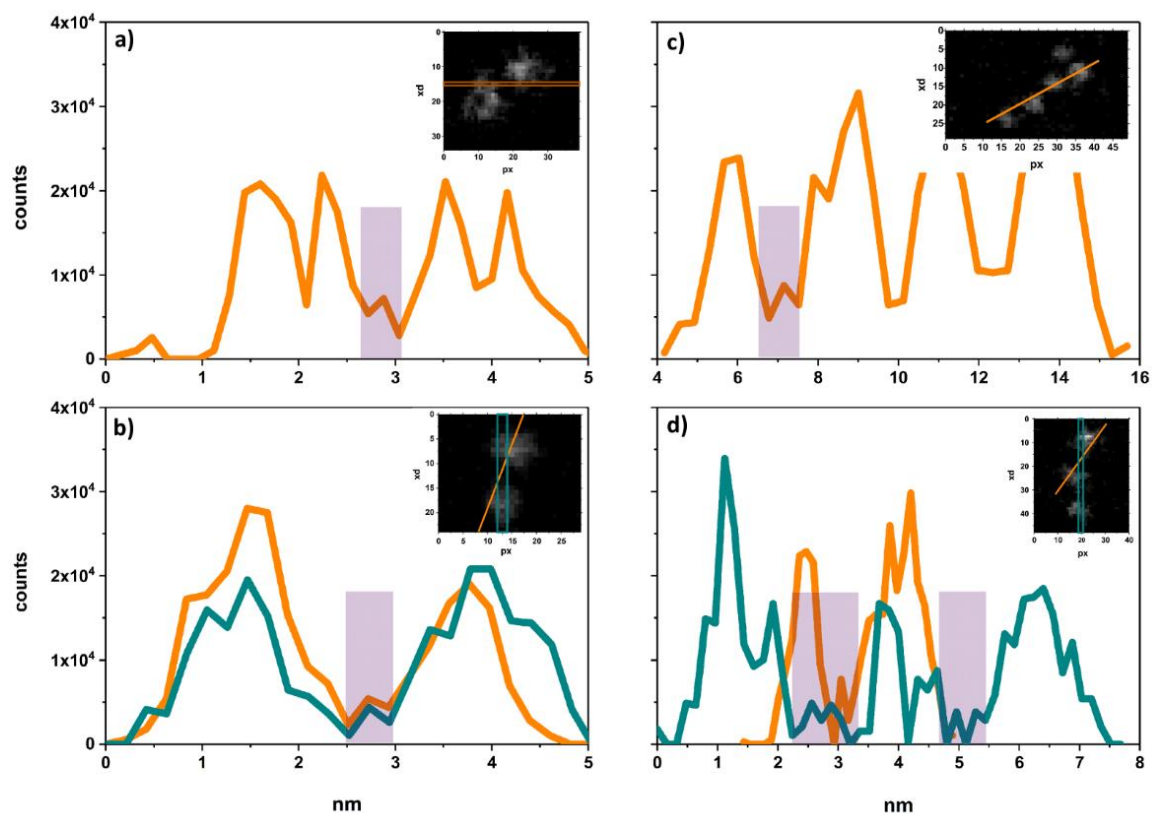
**Figure S4.** A core-loss spectrum of covalently-linked gold nanoclusters, accelerating voltage: 80kV. Core-loss spectra acquired by STEM-EELS from the region marked in a green rectangle. Energy-loss intensities of S-L (165 eV), C-K (284 eV), N-K (401 eV) and O-K (532 eV) were recorded which are characteristic features of the sample.



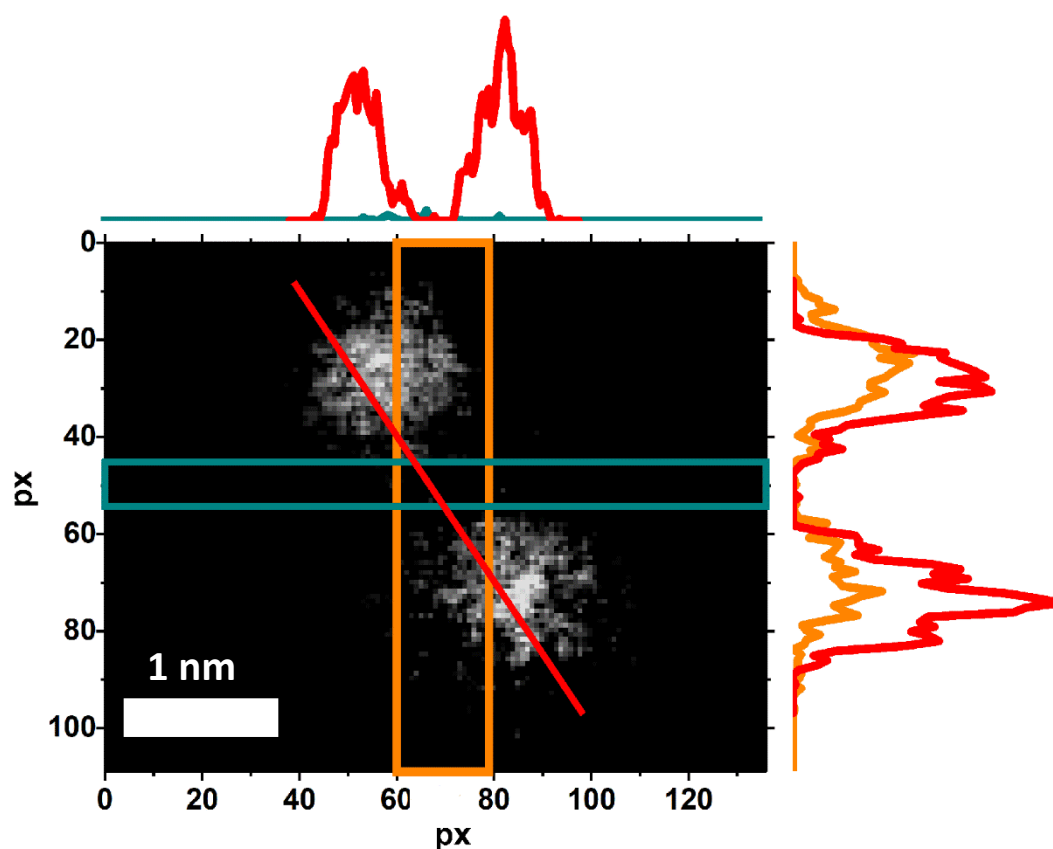
**Figure S5.** Logarithmic intensity plot of sulfur elemental map derived from the EELS spectrum.



**Figure S6.** (a)—(d) Atomic-level EELS mapping of gold superstructures. A set of yellow-coded sulfur maps of linked Au structures. The brightness and contrast of the images were adjusted.



**Figure S7.** (a)—(d) The enlarged cross-section profiles of sulfur intensities taken along the lines indicated in the inset images. The inset images are the same as the enlarged yellow coded images shown in S5(a)—(d), respectively.



**Figure S8.** Vertical (orange), horizontal (cyan) and diagonal (red) cross-section profiles of a dimer pair. The distance between nanoclusters indicates the possible bridge formation, however, no sulfur signal was detected, meaning that the clusters are either linked through the single dithiol molecule or the electron beam caused some irreversible changes to the structures.

## References

1. T. Lahtinen, E. Hulkko, K. Sokołowska, T. R. Tero, V. Saarnio, J. Lindgren, M. Pettersson, H. Häkkinen, and L. Lehtovaara, *Nanoscale*, 2016, **8**, 18665–18674.
2. K. Sokołowska, E. Hulkko, L. Lehtovaara, and T. Lahtinen, *J. Phys. Chem. C*, 2018, **122**, 12524–12533.