

Electronic Supplementary Information (ESI)

Taking a Different Road: Following Ag₂₅ and Au₂₅ Cluster Activation via *In Situ* Differential Pair Distribution Function Analysis

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Description of calculation and interpretation of Pearson correlation coefficients for similarity mapping of PDF data (For Figures 6 and 9)

The Pearson correlation coefficient is typically used to measure the extent of a linear association between two variables (j, k), where the value $r_{jk} = 1$ means a perfect positive correlation and the value $r_{jk} = -1$ means a perfect negative correlation. The r_{jk} can be calculated using equation 1 below for a give paired data $\{(j_1, k_1), (j_2, k_2), \dots, (j_n, k_n)\}$ that consist of n pairs.

$$r_{jk} = \frac{\sum_{i=1}^n (j_i - \bar{j})(k_i - \bar{k})}{\sqrt{\sum_{i=1}^n (j_i - \bar{j})^2} \sqrt{\sum_{i=1}^n (k_i - \bar{k})^2}} \quad \dots\dots\dots \text{Eq. 1}$$

where nn is the number of data point, j_i and k_i are the individual data points indexed with i , the \bar{j} is the mean of data set j and the \bar{k} is the mean of data set k .

Each PDF profile consists of \mathbf{R} in x-axis and $\mathbf{G}(\mathbf{r})$ in y-axis. To find the similarity between two PDF profiles (j, k) with the same number of data points (n), that is over similar \mathbf{R} -ranges, we calculated the Pearson correlation (r_{jk}) between the $\mathbf{G}(\mathbf{r})$ of one set PDF data at a given temperature (as j) and the $\mathbf{G}(\mathbf{r})$ of the second set of PDF data at a different temperature (as k) using

the equation above. The r_{jk} value obtained for each pair of PDF data is represented by a pixel in the Pearson correlation matrix which is drawn as a correlogram map. For many PDF datasets, one can use “PDF in the cloud” resource available on the website <https://pdfitc.org/login> to generate Pearson correlation matrices and corresponding correlogram maps. The “PDF in the cloud” site has a feature that enables the data set to be treated for different R-ranges of choice.

Each of the Pearson correlation matrix maps shows how similar datasets are to each other. A map is meant to be read like one would read a multiplication table, where any given square corresponds to correlation of the data for the temperature shown for that specific row and that specific column. The tiles in these maps generally represent how similar the PDF files at different temperatures are to one another based on a Pearson correlation coefficient calculation. Generally, it means that when the peaks of PDF plots collected at different temperatures overlap, you have higher correlation, and therefore a higher value for that box (with colour code on adjacent scale) on the graph.

For example, the whole diagonal shows correlations of one, since these will be the correlation of any given dataset to itself at the same temperature (as it is the same PDF, all the peaks should overlap exactly). It should be noted that PDF files will be considered somewhat dissimilar per the Pearson correlation coefficient even if the only difference is thermal expansion rather than any sort of phase change. However, in the absence of phase changes, the map appears to have a similar colour as you move across a row (or down a column, it is a symmetric matrix). When the data suddenly changes (for example, there is a structural phase transition) there will be a rapid change in color in the map at that point. As such, Pearson correlation matrices are a rapid way to look at large dataset to quickly find where (i.e., over which datasets) the sample is changing, and one can then focus on those regions for more detail about exact changes in that region of the temperature series.

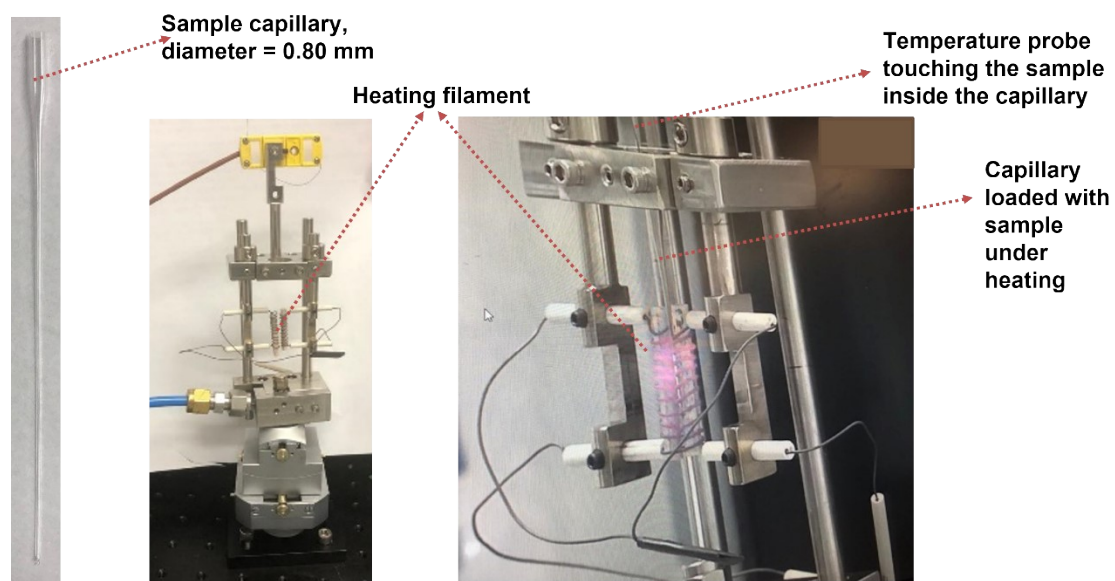


Figure S1. Set up for *in situ* heating at Brockhouse beamline, Canadian Light Source.

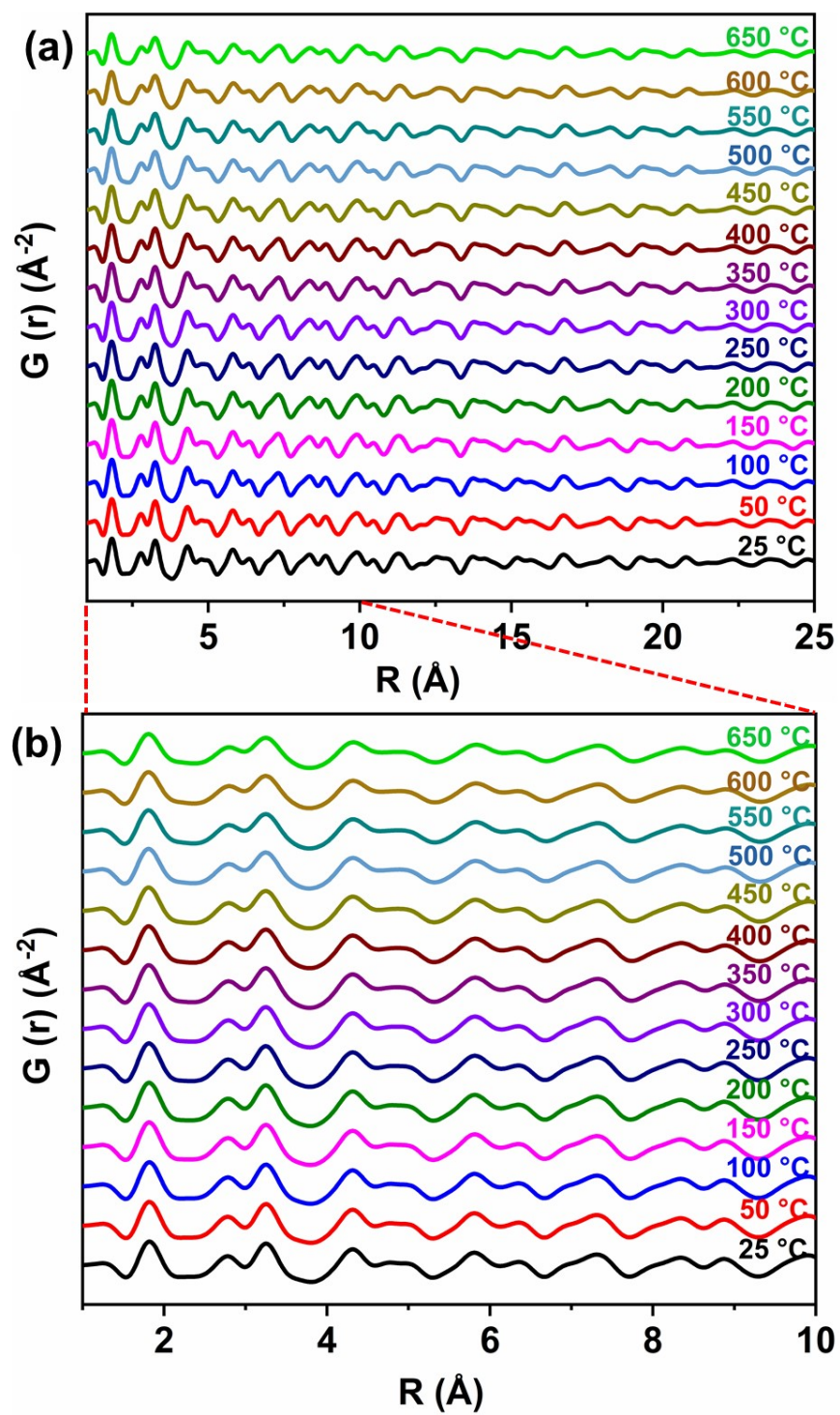


Figure S2. Atomic PDF profile of γ -alumina support under *in situ* heating at different temperatures over (a) long distance, and (b) short distance.

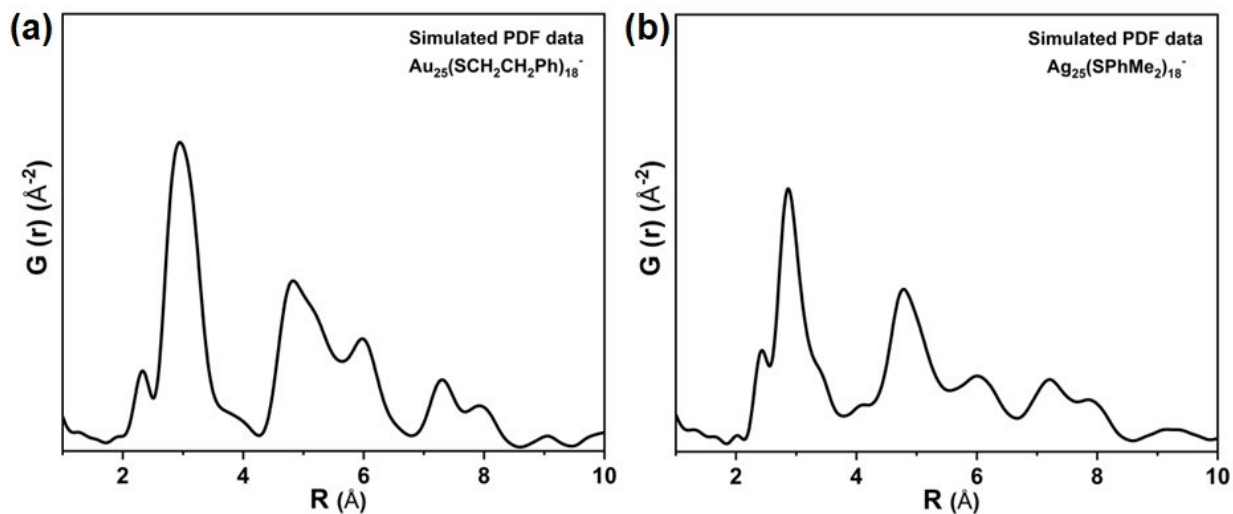


Figure S3. Simulated atomic PDF plots for (a) $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}^-$ and (b) $\text{Ag}_{25}(\text{SPhMe}_2)_{18}^-$ clusters from their respective SCXRD data reported in the literature.^{1,2}

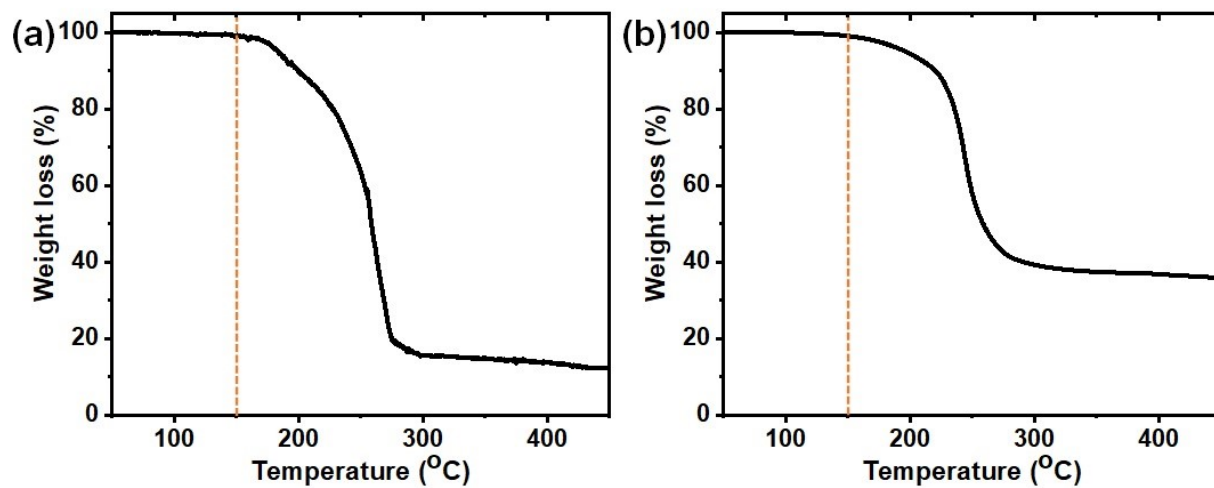


Figure S4. Thermogravimetric analysis profiles of (a) $\text{Au}_{25}(\text{11-MUA})_{18}^-$ and (b) $\text{Ag}_{25}(\text{SPhMe}_2)_{18}^-$ clusters.

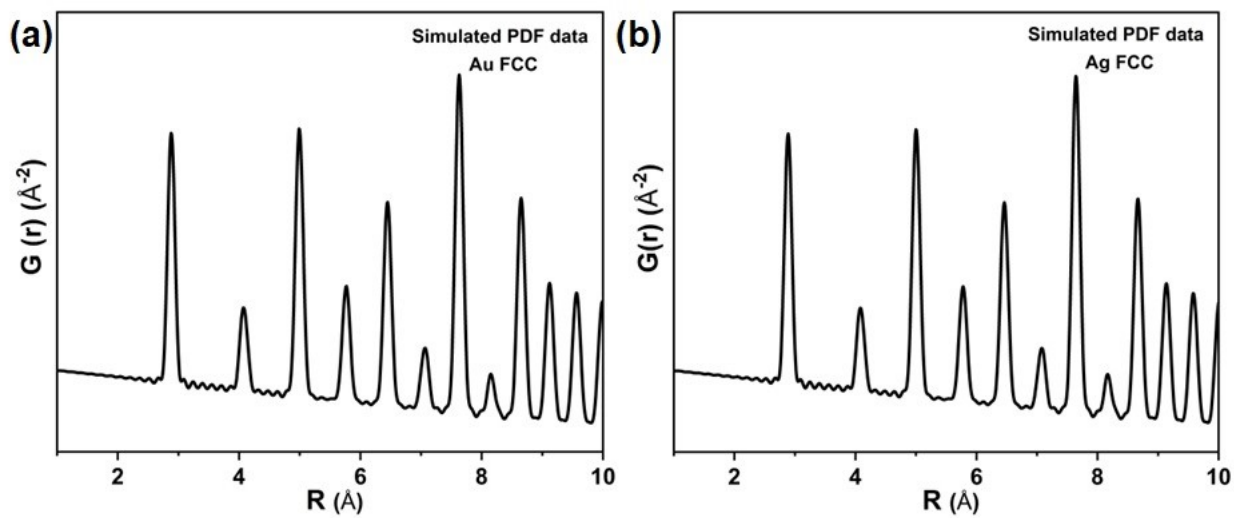


Figure S5. Simulated atomic PDF plot for (a) Au and (b) Ag, fcc models at higher Q_{\max} of 40\AA^{-1} to improve the signal-to-noise ratio.

References

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2. C.P. Joshi, M.S. Bootharaju, M.J. Alhilaly and O.M. Bakr, *J. Am. Chem. Soc.*, 2015, **137**, 11578.