

Supporting Information

New Evidence of the Bidentate Binding Mode in 3-MBA Protected Gold Clusters: Analysis of Aqueous 13–18 kDa Gold-Thiolate Clusters by HPLC-ESI-MS Reveals Special Compositions $\text{Au}_n(\text{3-MBA})_p$, ($n = 48 - 67$, $p = 26-30$)

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Table of Contents

1. Figure S1. Fine-structure in the electrospray negative ionization mode mass spectrometric analysis of the (67, 30), complex $[67, 30]^z$ in solution.
2. Figure S2. Electrospray positive ionization (ESI+) mass spectrometric analysis of the component identified as (67, 30), by HPLC-ESI-MS as in Figure 2.
3. Figure S3. ESI-MS Analysis of *GPV* sample preparation, under conditions wherein mainly the singly charged ($z = 1-$) ions are detected.
4. Figure S4. The polyacrylamide gel electrophoresis (PAGE) and HPLC analyses of *GPV* sample preparation.

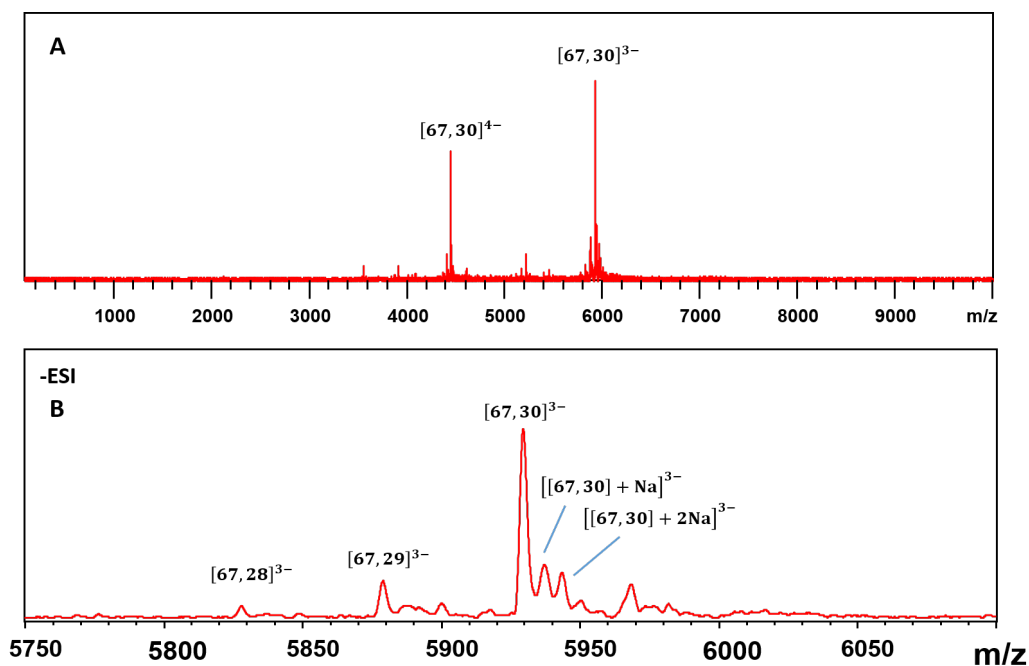


Figure S1. Fine-structure in the electrospray negative ionization mode mass spectrometric analysis of the (67, 30), complex $[67, 30]^z$ in solution. (A) The cluster can be detected intact, thus confirming its composition and (3-, 4-) charge states. (B) The expansion of 3- charge state peak, showing proposed assignment of adduct and fragment peaks. Under these conditions, the cluster is induced to fragment by loss of ligands (30-29-28-27) while maintaining its Au-atom count fixed at 67. Several less dominant minor peaks are identified as sodium adducts.

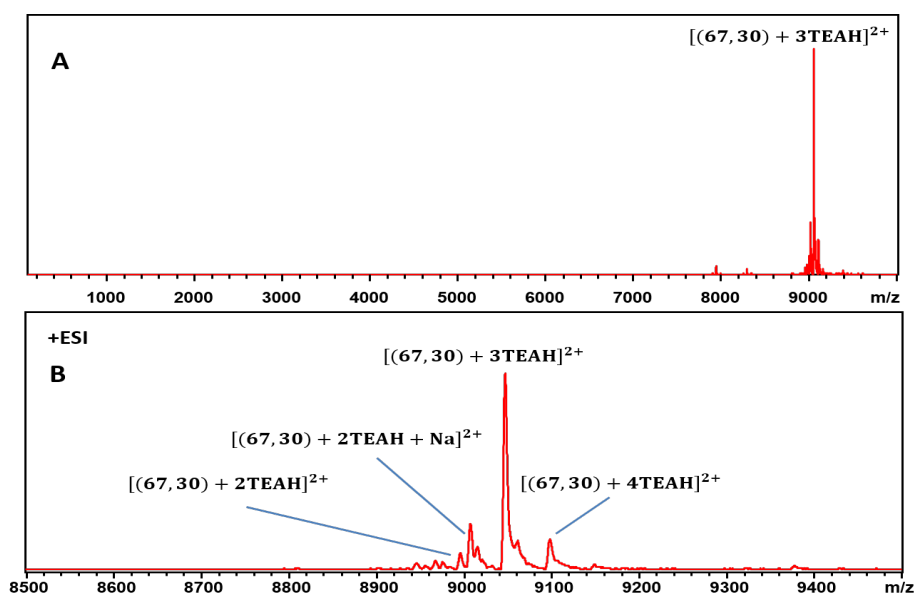


Figure S2. Electrospray positive ionization (ESI+) mass spectrometric analysis of the component identified as (67, 30), by HPLC-ESI-MS as in Figure 2. (A) The main peak is used to assign this composition, assuming 2+ charge state and three (3) triethylamine (TEA) adducts. (B) Close-up showing the assignment of features in the $z = 2+$ region. Note that other assignments preserve the (67, 30, q) label, where q designates the number of TEAH⁺ and Na⁺ adducts. The dominance of $q = 3$ peaks suggests the (67, 30) complex may have an intrinsic charge of (1⁻), i.e. $(67, 30)^{1-}$, as discussed in the text. (However, note also that the mass of 3x TEAH = 306 and 2x MBA = 306 also, which one therefore cannot distinguish at the resolution shown.)

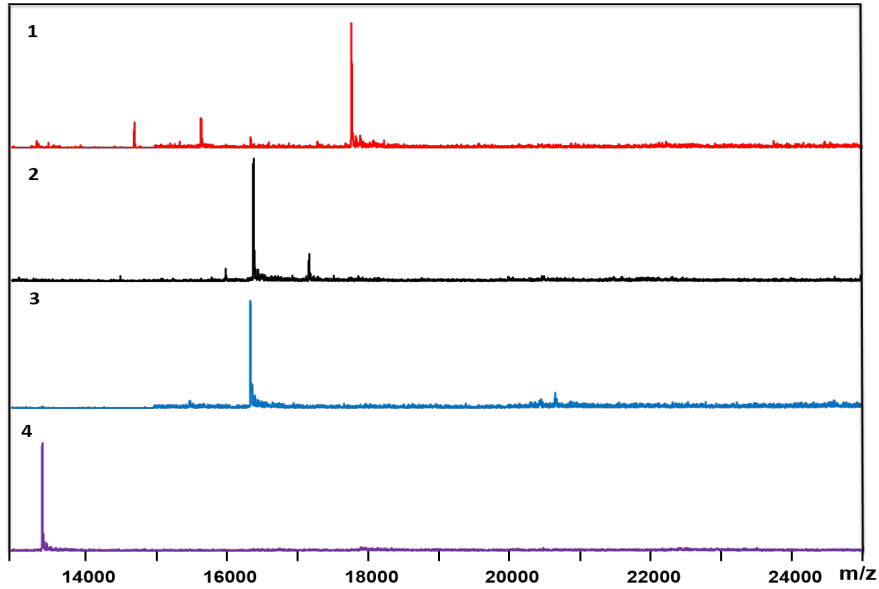


Figure S3. ESI-MS Analysis of GPV sample preparation, under conditions wherein mainly the singly charged ($z = 1$ -) ions are detected. Negative ionization mode used for analysis. The color-coded chromatographic peaks track with the correspondingly coded and numbered for singly charged mass spectra listed here with proposed compositions: (1, Red) (67, 30), 17.8 kDa; (2, Black) (60, 31), 16.6 kDa; (3, Blue) (60, 30), 16.4 kDa; and (4, Purple) (48, 26), 13.4 kDa.

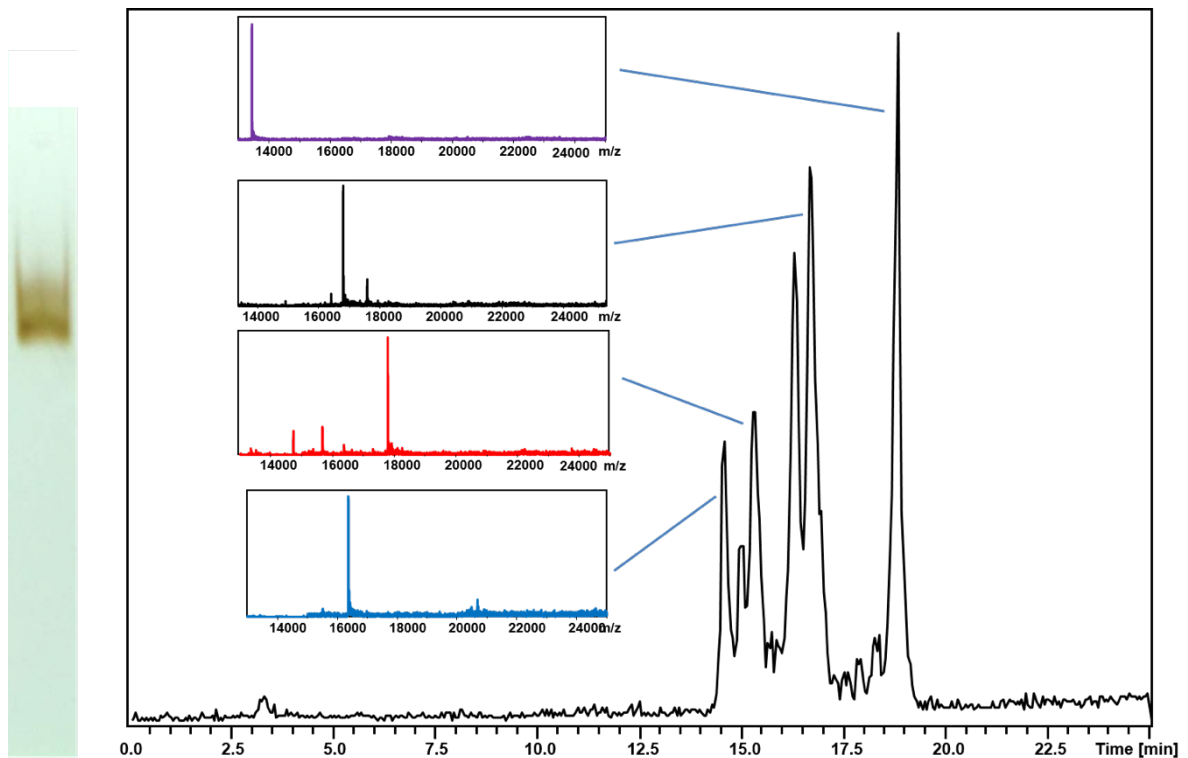


Figure S4. The polyacrylamide gel electrophoresis (PAGE) and HPLC analyses of GPV sample preparation. (Left) Photograph of the PAGE analysis image of the sample. (Right) HPLC chromatogram indicating correspondence to the mass spectra (inset) presented in Figure S3.