



Article

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 $Au_n(3\text{-MBA})_p$, ($n = 48\text{--}67$, $p = 26\text{--}30$)

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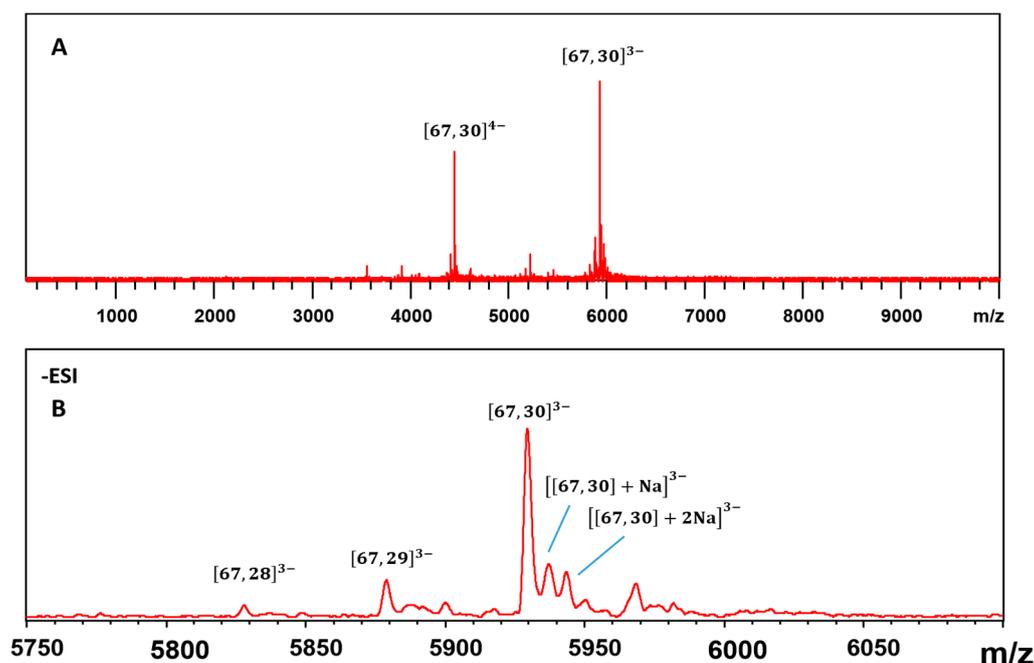


Figure S1. Fine-structure in the electrospray negative ionization mode mass spectrometric analysis of the (67, 30) complex (67, 30)^{z-} in solution. **(A)** The cluster can be detected intact, thus confirming its composition and (3-, 4-) charge states. **(B)** The expansion of 3- charge state peak, 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.

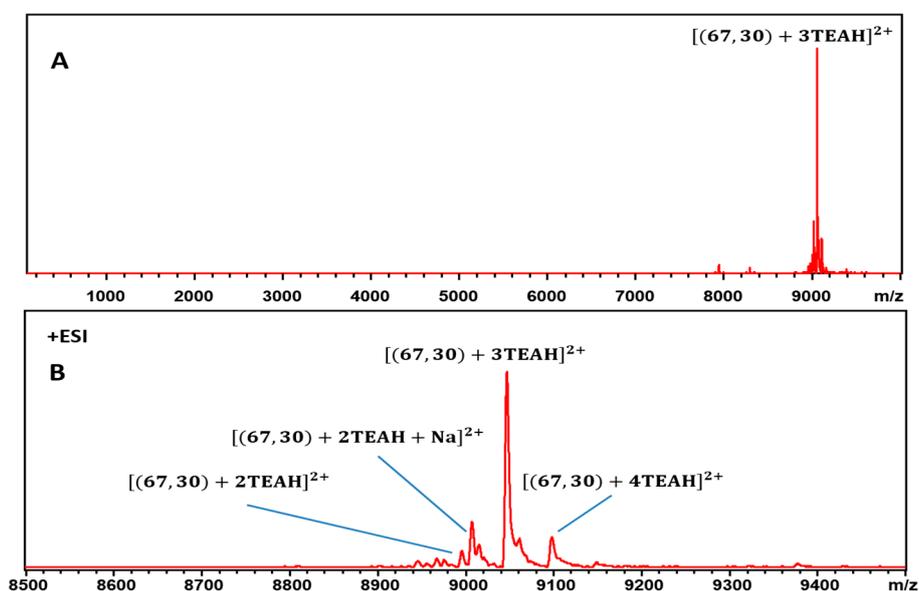


Figure S2. Electrospray positive ionization (ESI+) mass spectrometric analysis of the component identified as (67, 30), by HPLC-ESI-MS as in Figure 2. **(A)** The main peak is used to assign this composition, assuming 2+ charge state and three (3) triethylamine (TEA) adducts. **(B)** Close-up showing 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.)

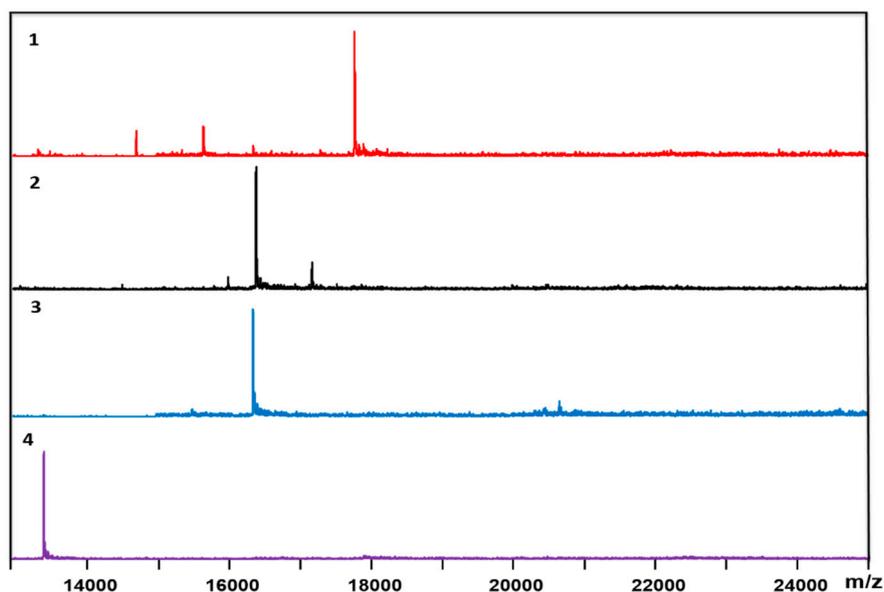


Figure S3. ESI-MS Analysis of GPV sample preparation, under conditions wherein mainly the singly charged ($z = 1$ -) ions are detected. Negative ionization mode used for analysis. The color-coded chromatographic peaks track with the correspondingly coded and numbered for singly charged mass spectra listed 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.

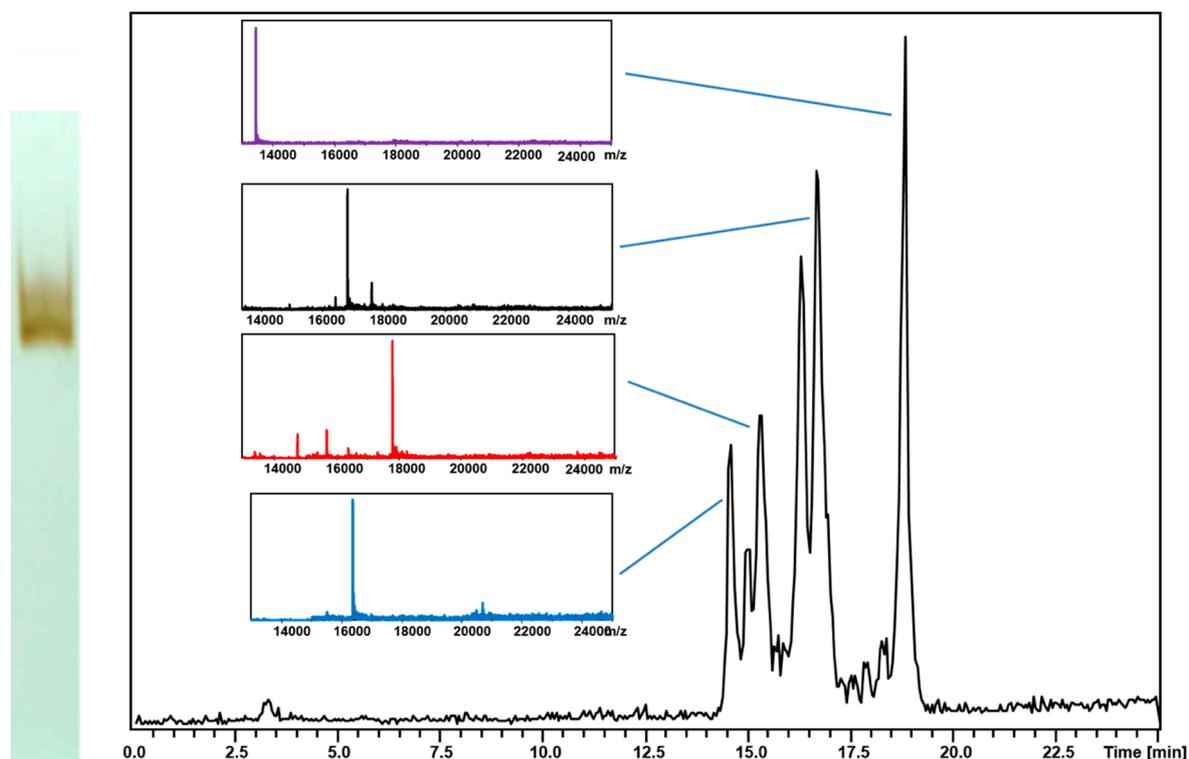


Figure S4. The polyacrylamide gel electrophoresis (PAGE) and HPLC analyses of GPV sample preparation. **(Left)** Photograph of the PAGE analysis image of the sample. **(Right)** HPLC chromatogram indicating correspondence to the mass spectra (inset) presented in Figure S3.



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