

## Supporting Information

### Digestive Ripening Yields Atomically Precise Au Nanomolecules.

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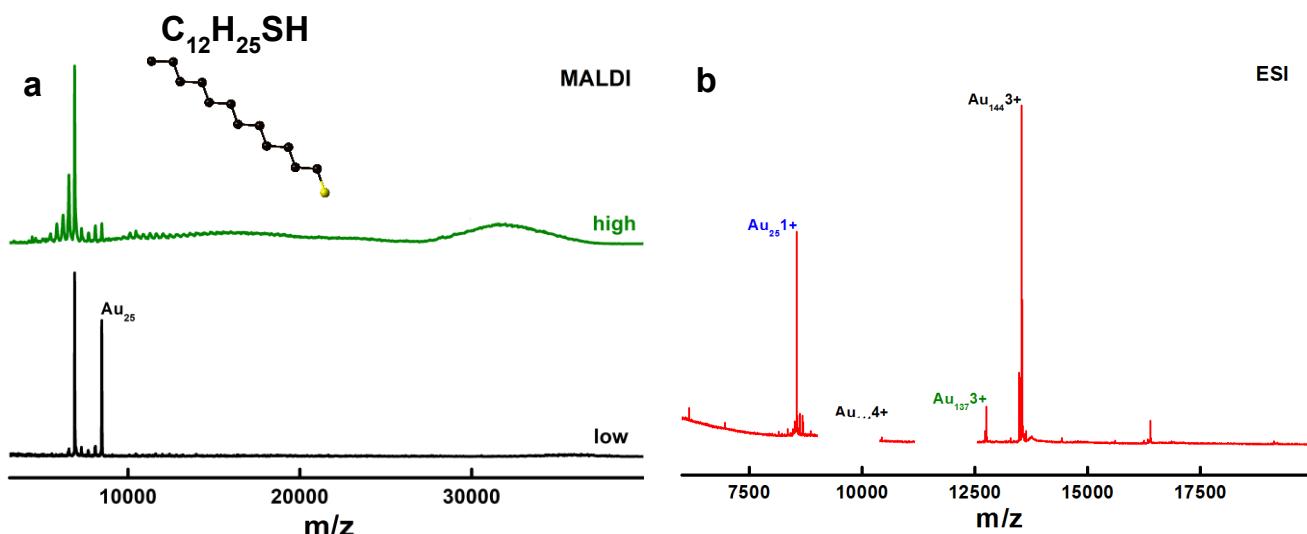
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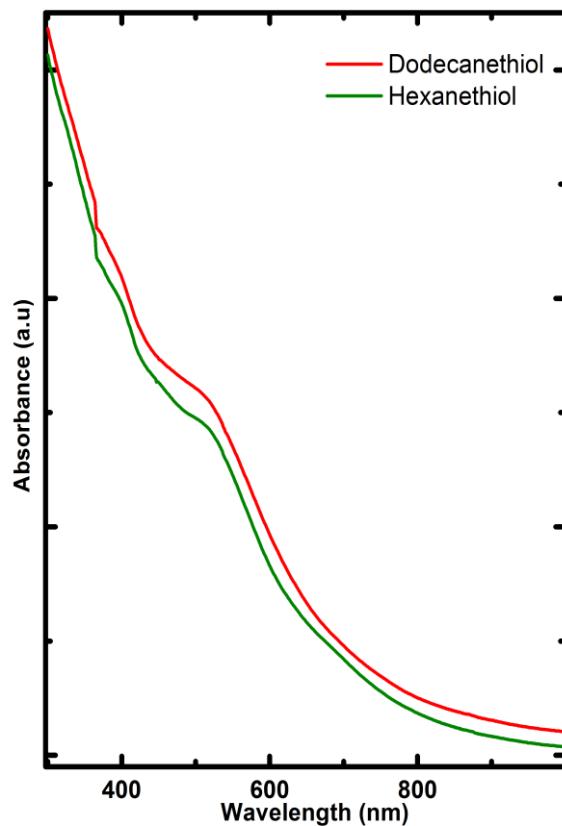
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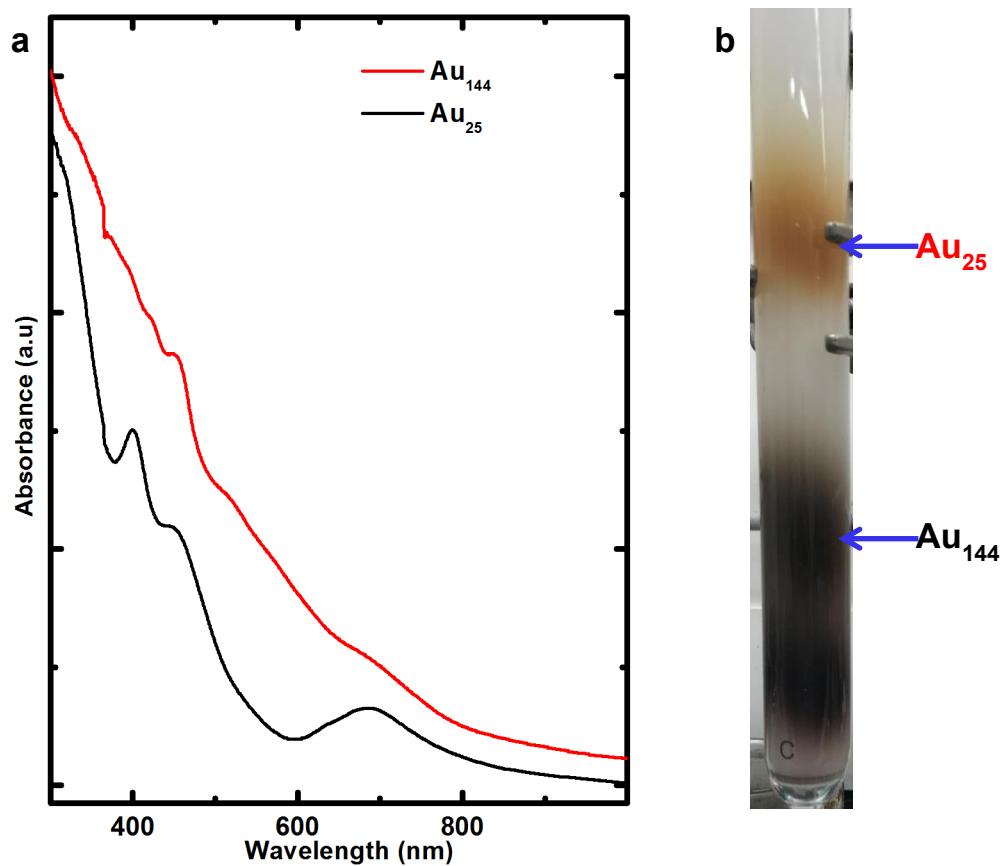
1. **Figure S1.** Dodecanethiol protected atomically precise gold nanomolecules synthesized using digestive ripening method. a) MALDI-MS data showing high (green) and low (black) laser. (b) ESI-MS data showing the presence of  $\text{Au}_{144}$ ,  $\text{Au}_{137}$  and  $\text{Au}_{25}$  species in the product.
2. **Figure S2.** UV-vis plot of the digestive ripening synthesis products protected by hexanethiol and dodecanethiol.
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4. **Figure S4.** Dodecanethiol protected gold nanomolecules a) UV-vis plot of  $\text{Au}_{144}(\text{SR})_{60}$  (with  $\text{Au}_{137}(\text{SR})_{54}$ ) and  $\text{Au}_{25}(\text{SR})_{18}$  after SEC separation. b) Photograph of the SEC column separation performed on final product of digestive ripening synthesis.
5. **Figure S5.** Hexanethiol protected gold nanomolecules after SEC a) MALDI-MS spectra showing 30 kDa species ( $\text{Au}_{144}(\text{SR})_{60}$  &  $\text{Au}_{137}(\text{SR})_{54}$ ) and  $\text{Au}_{25}(\text{SR})_{18}$  (7 kDa). b) ESI-MS spectra showing 30 kDa species ( $\text{Au}_{144}(\text{SR})_{60}$  &  $\text{Au}_{137}(\text{SR})_{54}$ ) and  $\text{Au}_{25}(\text{SR})_{18}$  (7 kDa). \*fragment peak.
6. **Figure S6.** Dodecanethiol protected gold nanomolecules after SEC a) MALDI-MS spectra showing 30 kDa species ( $\text{Au}_{144}(\text{SR})_{60}$  &  $\text{Au}_{137}(\text{SR})_{54}$ ) and  $\text{Au}_{25}(\text{SR})_{18}$  (8 kDa). b) ESI-MS spectra showing 30 kDa species ( $\text{Au}_{144}(\text{SR})_{60}$  &  $\text{Au}_{137}(\text{SR})_{54}$ ) and  $\text{Au}_{25}(\text{SR})_{18}$  (8 kDa). \*fragment peak.
7. **Figure S7.** High (green) and low (black) laser MALDI-MS data of dodecanethiol protected gold nanomolecules comparing 2 methods (a) Digestive Ripening (b) Brust method.
8. **Figure S8.** MALDI-MS and ESI-MS data of hexanethiol protected gold nanomolecules synthesized using digestive ripening synthesis method with ToABr as phase transfer agent. (\* marked peaks are impurity from previous sample).



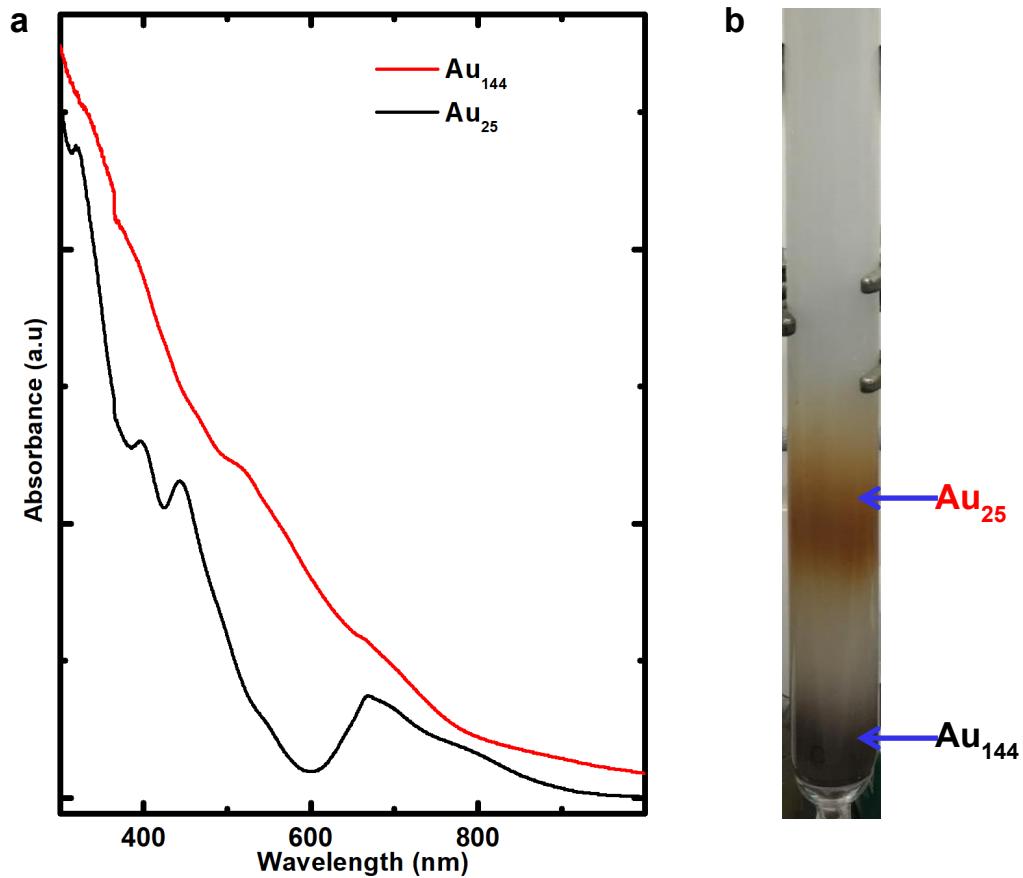
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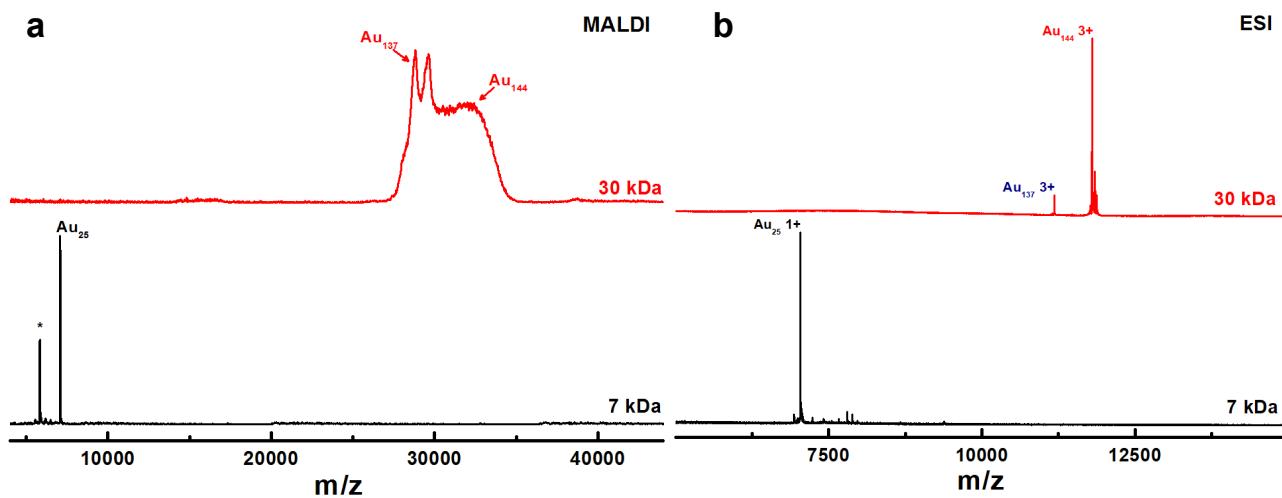
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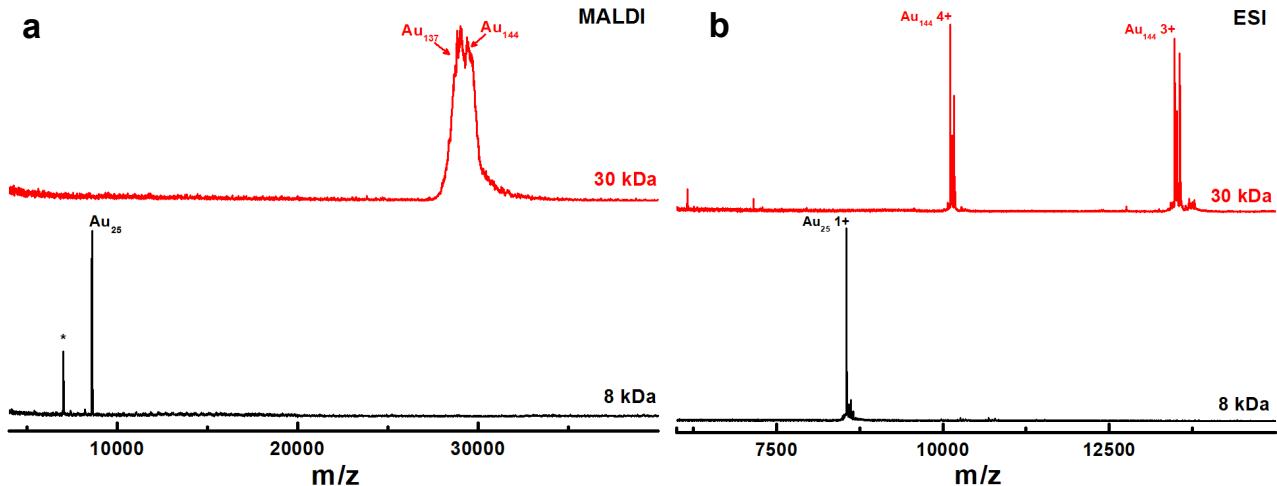
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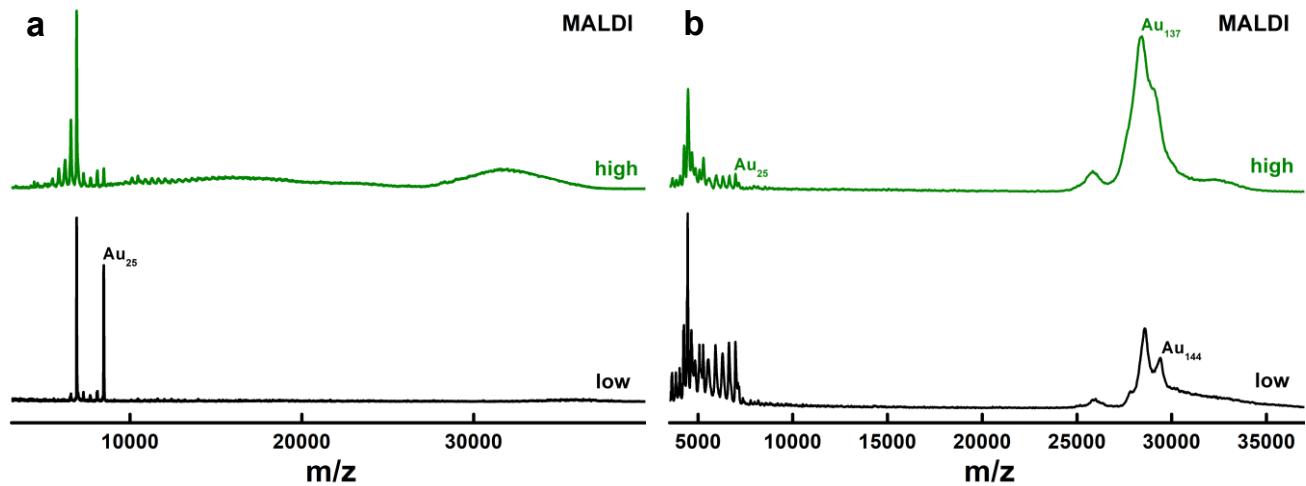
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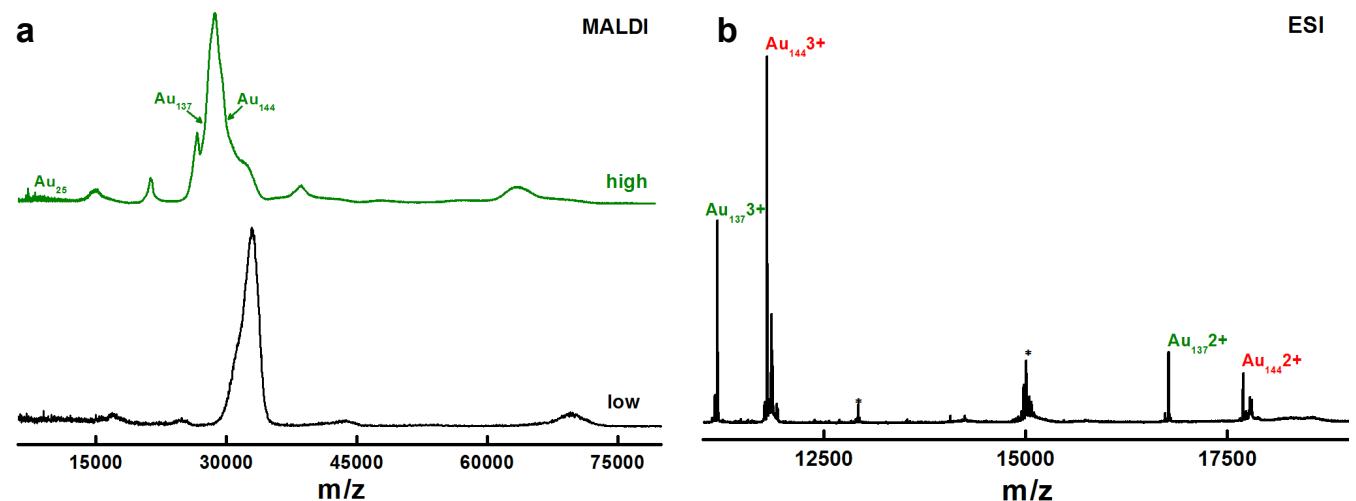
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