SUPPLEMENTARY MATERIAL

Enhancing Catalytic Properties of Ligand-Protected Gold -Based 25-Metal Atom Nanoclusters by Silver Doping

Ricca Rahman Nasaruddin*[,a,b], Max J. Hülsey[a] and Jianping Xie,*[,a]

[a]*Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117585 (Singapore).*

[b]*Department of Biotechnology Engineering, Kuliyyah of Engineering, International Islamic University Malaysia, 53100 Jalan Gombak, Kuala Lumpur, Malaysia (current affiliation)*

**Corresponding Authors: riccanasaruddin@iium.edu.my (R.R. Nasaruddin) and chexiej@nus.edu.sg (J. Xie)*

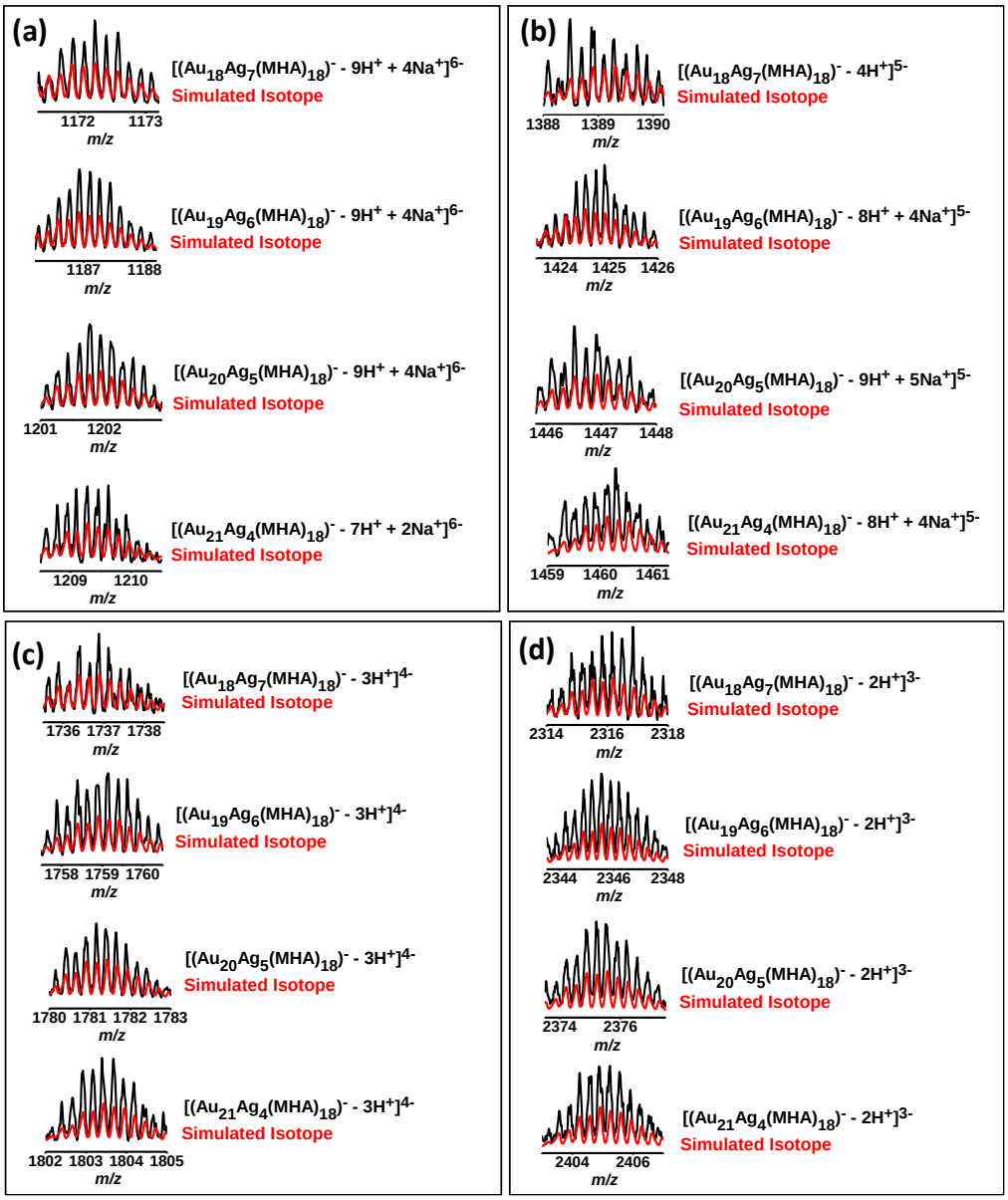

Fig. S1 ESI mass spectra and simulated isotope patterns for $Au_{18\text{-}21}Ag_{7\text{-}4}(MHA)_{18}$ NCs with (a) z = 6-, (b) z = 5-, (c) z = 4- and (d) z = 3-.

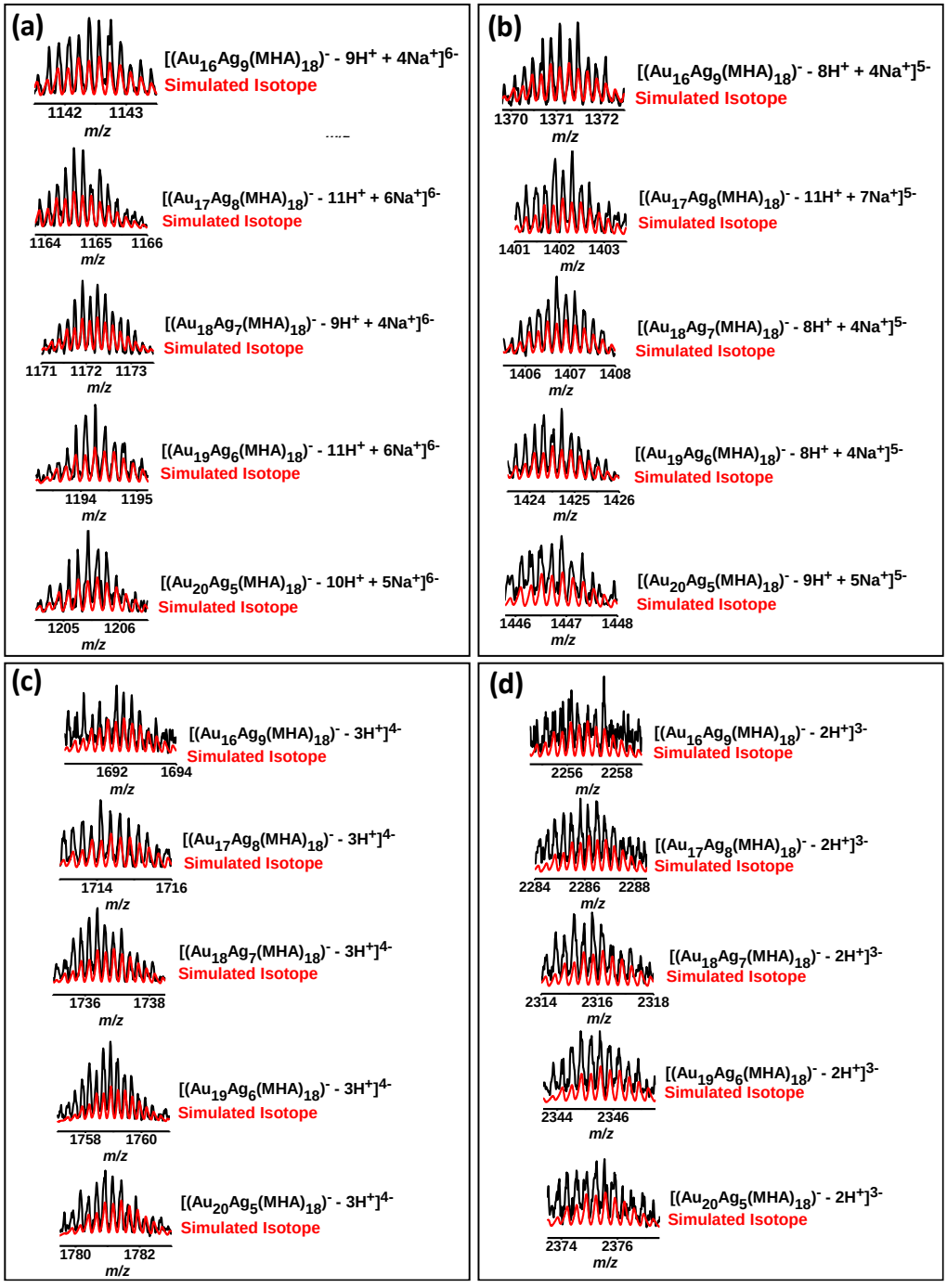

Fig. S2 ESI mass spectra and simulated isotope patterns for $Au_{16\text{-}20}Ag_{9\text{-}6}(MHA)_{18}$ NCs with (a) *z* = 6-, (b) *z* = 5-, (c) *z* = 4- and (d) *z* = 3-.

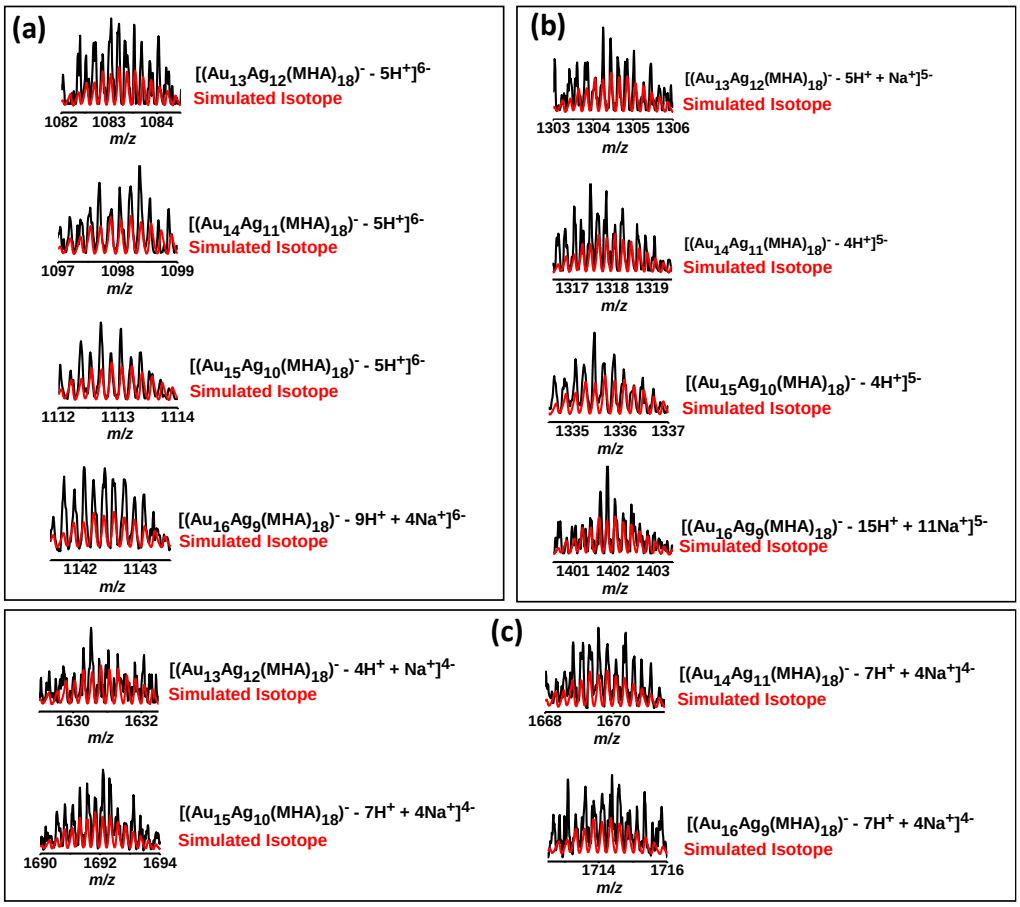

Fig. S3 ESI mass spectra and simulated isotope patterns for $Au_{13\text{-}16}Ag_{9\text{-}6}(MHA)_{18}$ NCs with (a) *z* = 6-, (b) *z* = 5- and (c) *z* = 4-.

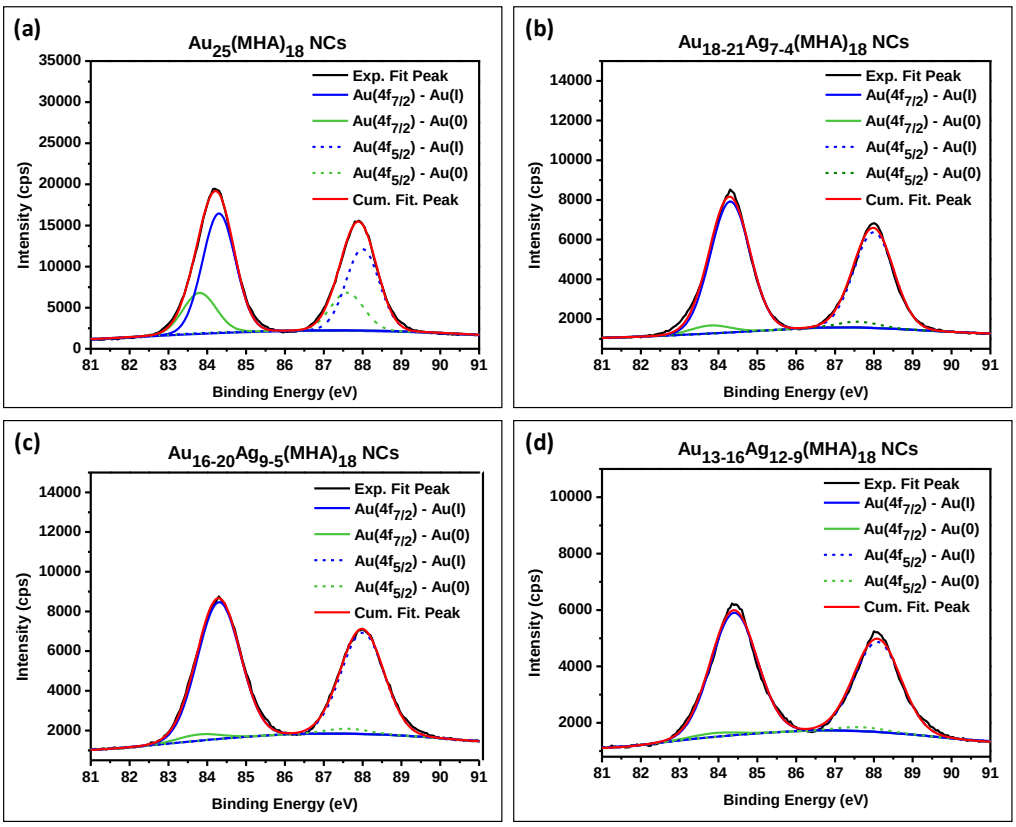

Fig. S4 Deconvoluted XPS spectra for Au (4f) of (a) $Au_{25}(MHA)_{18}$, (b) $Au_{18\text{-}21}Ag_{7\text{-}4}(MHA)_{18}$, (c) $Au_{16\text{-}20}Ag_{9\text{-}5}(MHA)_{18}$ and (d) $Au_{13\text{-}16}Ag_{12\text{-}9}(MHA)_{18}$ NCs.

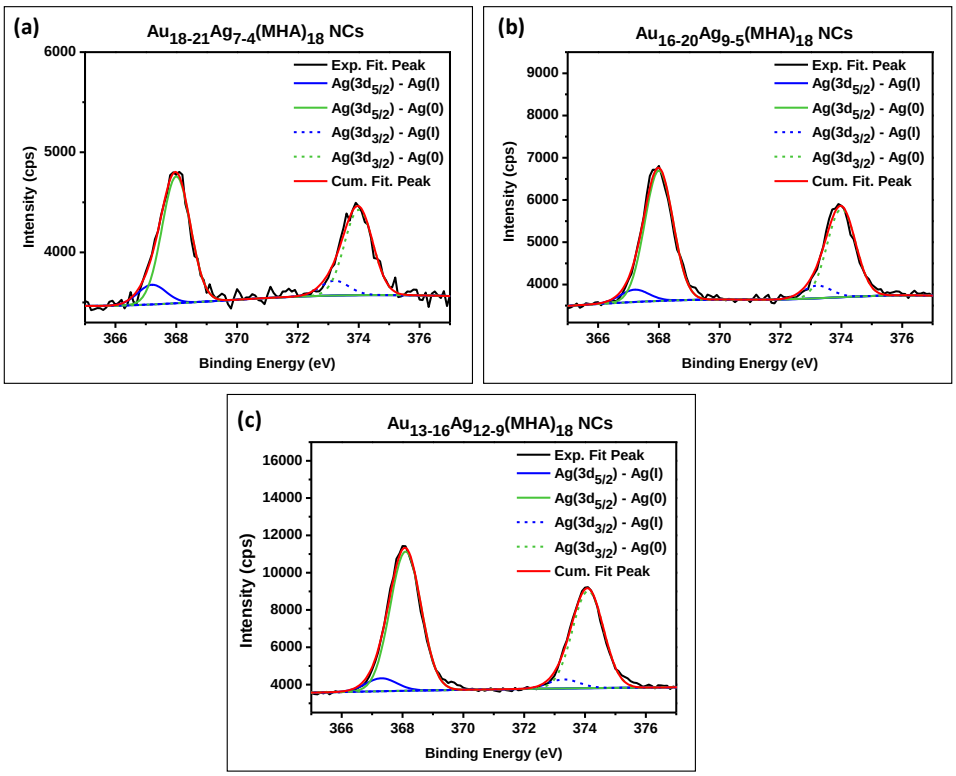

Fig. S5 Deconvoluted XPS spectra for Ag(3d) of (a) $Au_{18-21}Ag_{7-4}(MHA)_{18}$ NCs, (b) $Au_{16-20}Ag_{9-5}(MHA)_{18}$ NCs and (c) $Au_{13-16}Ag_{12-9}(MHA)_{18}$ NCs.

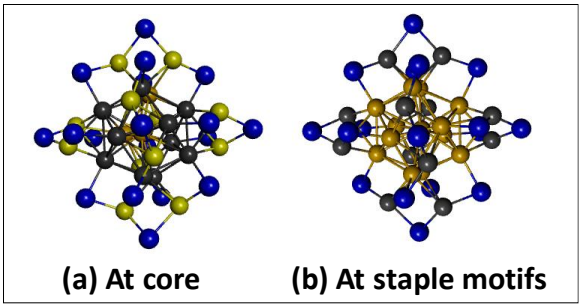

Fig. S6 Proposed location of silver (Ag) dopants in $Au_{25-x}Ag_x(MHA)_{18}$ NCs

Table S1 Hirshfeld charge analysis of different $Au_{25-x}Ag_x(SCH_3)_{18}$ for gold or silver atoms at different positions in the nanocluster.

Average charge	**$Au_{25}(SCH_3)_{18}$**	**$Au_{19}Ag_6(SCH_3)_{18}$**	**$Au_{13}Ag_{12}(SCH_3)_{18}$**
Central Atom	0.032	0.010	-0.015
Middle	0.068	0.078	0.088
Staple Motif	0.150	0.157	0.163
Average charge Au	0.106	0.119	0.150
Average charge Ag	N.A.	0.093	0.088