Electronic Supplementary Material (ESI) for ChemComm.

Supporting Materials

Facile Synthesis of Water-Soluble $Au_{25-x}Ag_x$ Nanoclusters Protected by Mono- and Bi-Thiolate Ligands

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EXPERIMENTAL SECTION

Materials. Ultrapure water (18.2 MΩ) was used in this study. All glassware and magnetic stir bars were washed with *aqua regia*, and rinsed with ethanol and ultrapure water. The following chemicals were used as received: Hydrogen tetrachloroaurate (III) hydrate ($HAuCl_4 \cdot 3H_2O$) from Alfa Aesar; sodium hydroxide (NaOH) and silver nitrate ($AgNO_3$) from Merck; 6-mercaptohexanoic acid (MHA), 8-mercaptooctanoic acid (MOA), 11-mercaptoundecanoic acid (MUA), cysteamine hydrocholoride (Cystm), 2-mercaptoethanol (MetH), and sodium borohydride ($NaBH_4$), from Sigma-Aldrich.

Instrumentation. UV-vis absorption spectra were recorded on a Shimadzu UV-1800 spectrometer. The molecular formulas of the as-synthesized NCs were determined by electrospray ionization (ESI) mass spectrometry on a Bruker microTOF-Q system. Transmission electron microscopy (TEM) images were obtained on a JEOL JEM 2010 microscope operating at 200 kV. X-ray photoelectron spectroscopy (XPS) was conducted on a Kratos AXIS Ultra^{DLD} spectrometer.

Synthesis of mono-thiolate-protected $Au_{25-x}Ag_x$ NCs. Mono-thiolate-protected $Au_{25-x}Ag_x$ NCs were synthesized according to our recent developed NaOH-mediated $NaBH_4$ reduction method with minor modifications. In a typical synthesis of MHA-protected $Au_{25-x}Ag_x$ NCs, an aqueous solution of MHA (5 mM, 2 mL) was first mixed with water (2.35 mL), followed by the introduction of a mixture (0.25 mL) of $HAuCl_4$ (20 mM) and $AgNO_3$ (20 mM) with different feeding ratios of Au^{3+}/Ag^+ or $R_{Au/Ag}$ (24/1, 22/3, 18/7, 16/9, and 14/11) under rigorous stirring, leading to the formation of MHA-Au(I)/Ag(I) complexes. Aqueous solutions of NaOH (1 M, 0.3 mL) and $NaBH_4$ (~112 mM, 0.1 mL, prepared by dissolving 43 mg of $NaBH_4$ powder in NaOH solution (10 mL, 0.2 M)) were then separately introduced to the reaction mixture. The MHA-protected $Au_{25-x}Ag_x$ NCs were collected after 3 h of reaction. MHA-protected $Au_{25-x}Ag_x$ NCs synthesized by using different feeding $R_{Au/Ag}$ (24/1, 22/3, 18/7, 16/9, and 14/11) were referred to as NC 1-5. When the volume of NaOH solution was varied from 0.3 to 0.08 mL, and the other synthetic conditions were kept as constant, we can produce $Au_{25-x}Ag_x(MOA)_{18}$ and $Au_{25-x}Ag_x(MUA)_{18}$ NCs. It should be noted that the MUA was dissolved in ethanol.

Synthesis of bi-thiolate-protected $Au_{25-x}Ag_x$ NCs. Bi-thiolate-protected $Au_{25-x}Ag_x$ NCs were synthesized by keeping all the experimental conditions unchanged except for the introduction of the second thiolate ligand. In a typical synthesis, the total volume of thiolate ligands was kept at 2 mL, and the amount of MHA (from 1.75, 1.5, 1.25, to 1 mL) and MetH (from 0.25, 0.5, 0.75, to 1 mL) was gradually adjusted. MHA/MetH-protected $Au_{25-x}Ag_x$ NCs with different ligand and/or metal proportions can be obtained. $Au_{25-x}Ag_x(MHA/Cystm)_{18}$ NCs were prepared by using the same strategy.

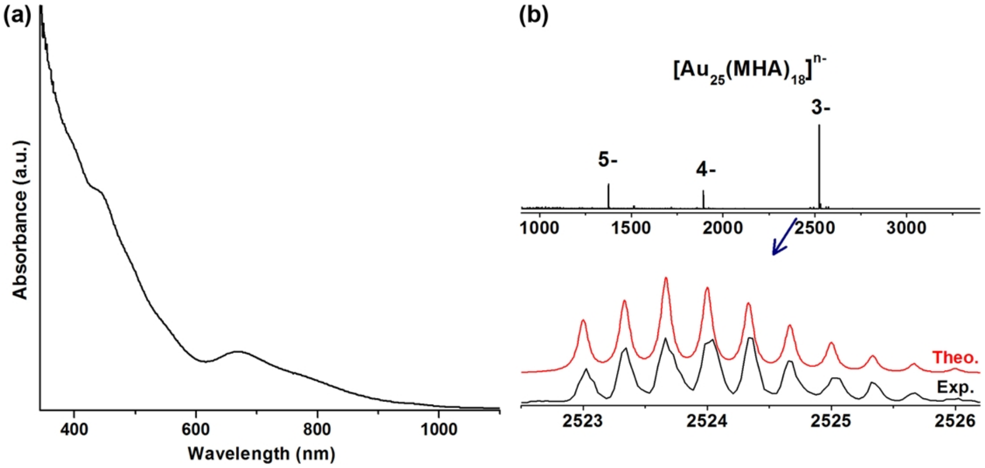

Figure S1. (a) UV-vis absorption and (b) ESI mass spectra of the as-synthesized MHA-protected Au_{25} NCs. The lower panel in (b) shows the isotope patterns of $[Au_{25}(MHA)_{18}\text{-}2H]^{3-}$ acquired theoretically (red) and experimentally (black).

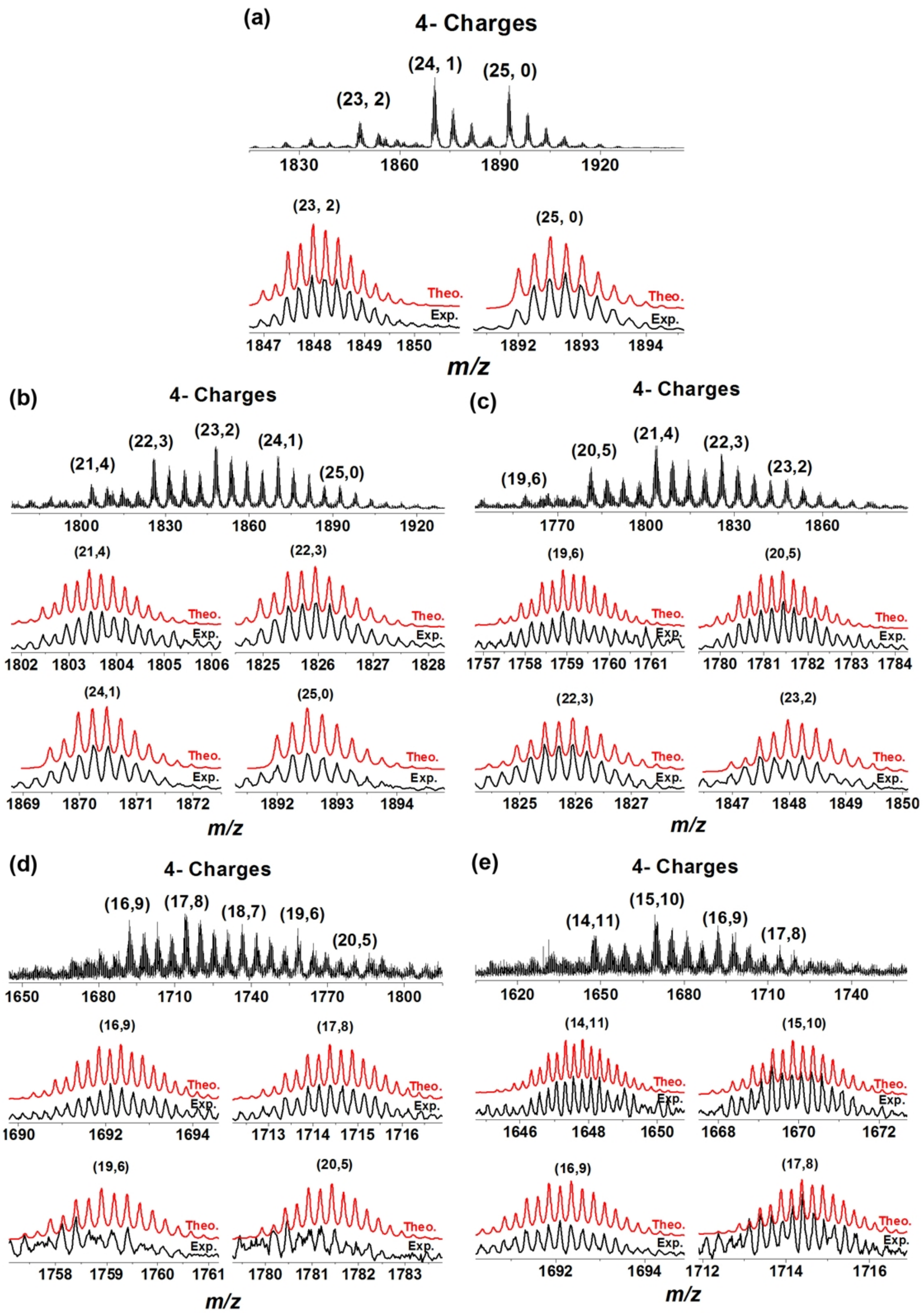

Figure S2. Zoom-in ESI mass spectra and representative isotope patterns (theoretical / red and experimental / black) of the MHA-protected $Au_{25-x}Ag_x$ NCs carrying 4- charges: (a) **NC-1**, (b) **NC-2**, (c) **NC-3**, (d) **NC-4**, and (e) **NC-5**. The numbers within the bracket are the number of Au and Ag atoms in $Au_{25-x}Ag_x$ NCs. For example, (21,4) is denoted as $Au_{21}Ag_4$ NC species.

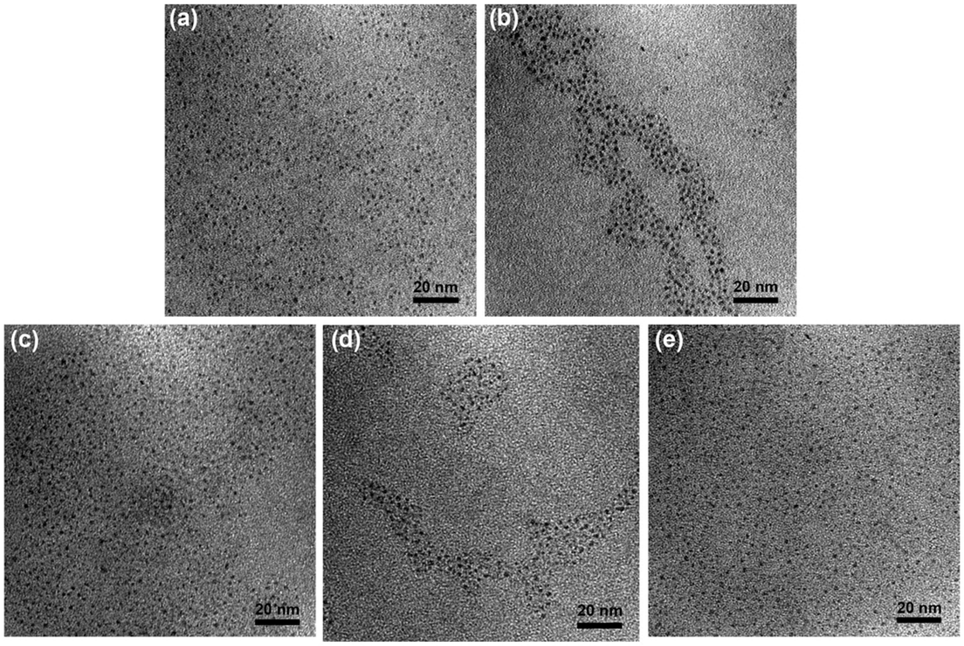

Figure S3. Representative TEM images of the as-synthesized MHA-protected $Au_{25-x}Ag_x$ NCs: (a) **NC-1**, (b) **NC-2**, (c) **NC-3**, (d) **NC-4**, and (e) **NC-5**.

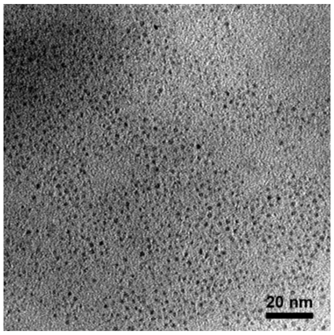

Figure S4. A representative TEM image of the as-synthesized $Au_{25}(MHA)_{18}$ NCs.

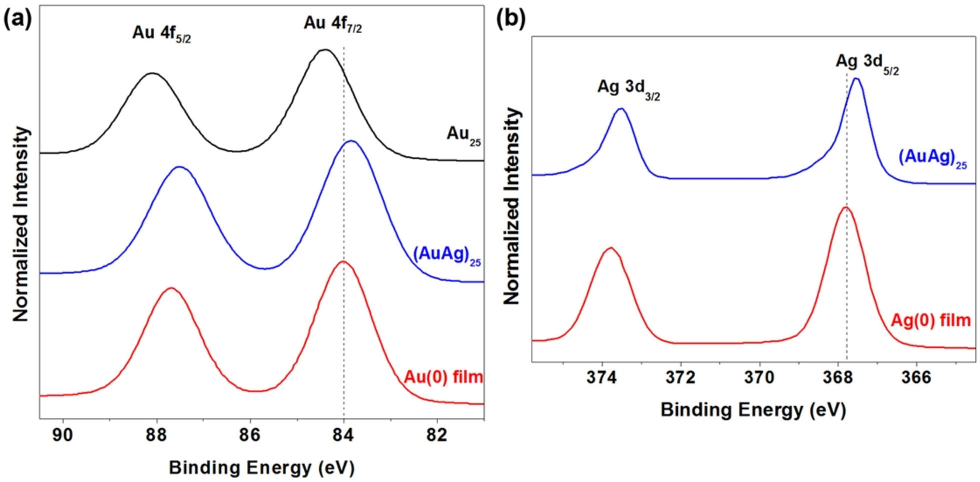

Figure S5. XPS spectra of (a) Au 4f species of MHA-protected Au_{25} NCs, MHA-protected $Au_{25-x}Ag_x$ NCs, and Au(0) film, and (b) Ag 3d species of MHA-protected $Au_{25-x}Ag_x$ NCs and Ag(0) film.

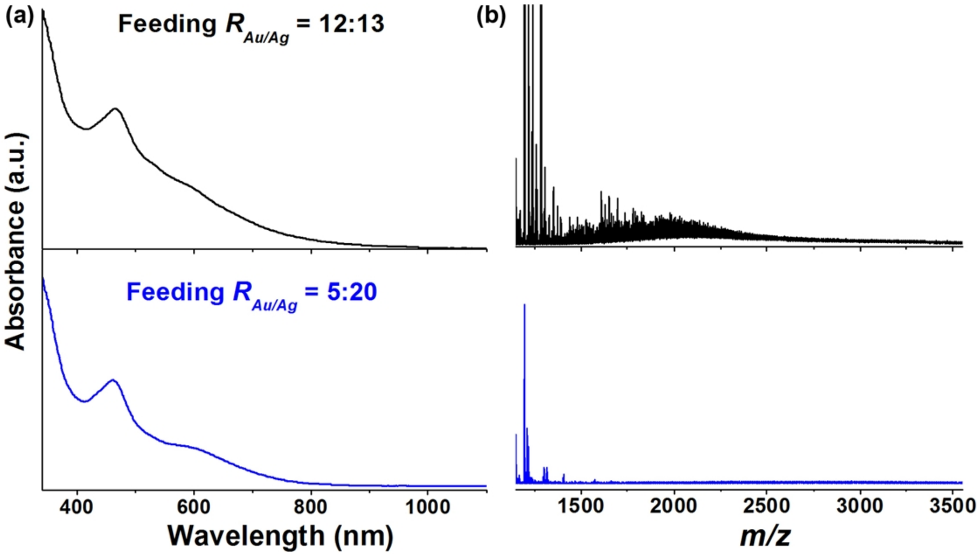

Figure S6. (a) UV-vis absorption and (b) ESI mass spectra of the MHA-protected AuAg NCs synthesized with the feeding $R_{Au/Ag}$ of 12/13 (upper panel, black lines) and 5/20 (lower panel, blue lines).

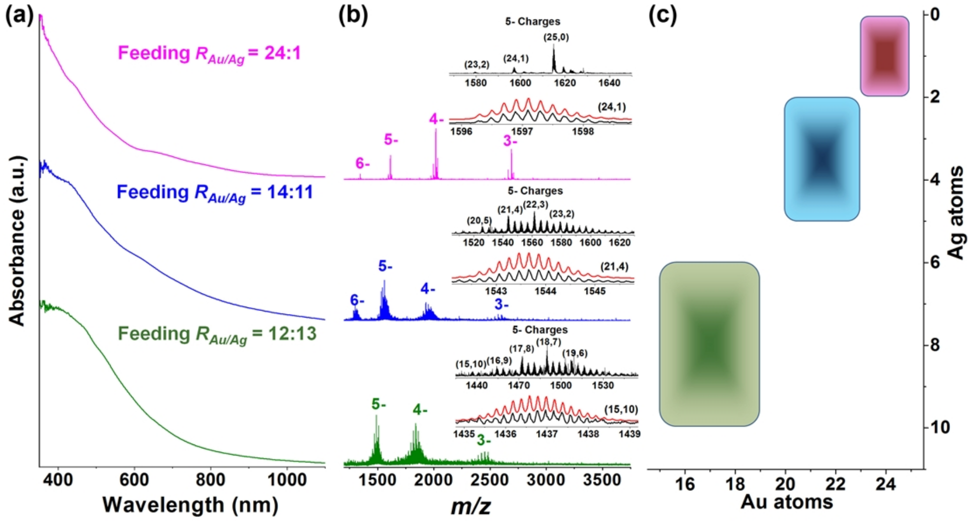

Figure S7. (a) UV-vis absorption spectra, (b) ESI mass spectra, and (c) the compositional distributions of MOA-protected $Au_{25-x}Ag_x$ NCs prepared at the feeding $R_{Au/Ag}$ of 24/1 (pink), 14/11 (blue), and 12/13 (green). Insets in (b) are zoom-in ESI spectra of 5-charged species of the as-synthesized AuAg NCs (upper panel) and representative isotope patterns (lower panel) acquired theoretically (red) and experimentally (black). (c) indicates that the as-synthesized MOA-protected $Au_{25-x}Ag_x$ NCs have different metal compositions: $Au_{23-25}Ag_{2-0}$ NCs ($R_{Au/Ag}$=24/1, pink), $Au_{20-23}Ag_{5-2}$ NCs ($R_{Au/Ag}$=14/11, blue), and $Au_{15-19}Ag_{10-6}$ NCs ($R_{Au/Ag}$=12/13, green).

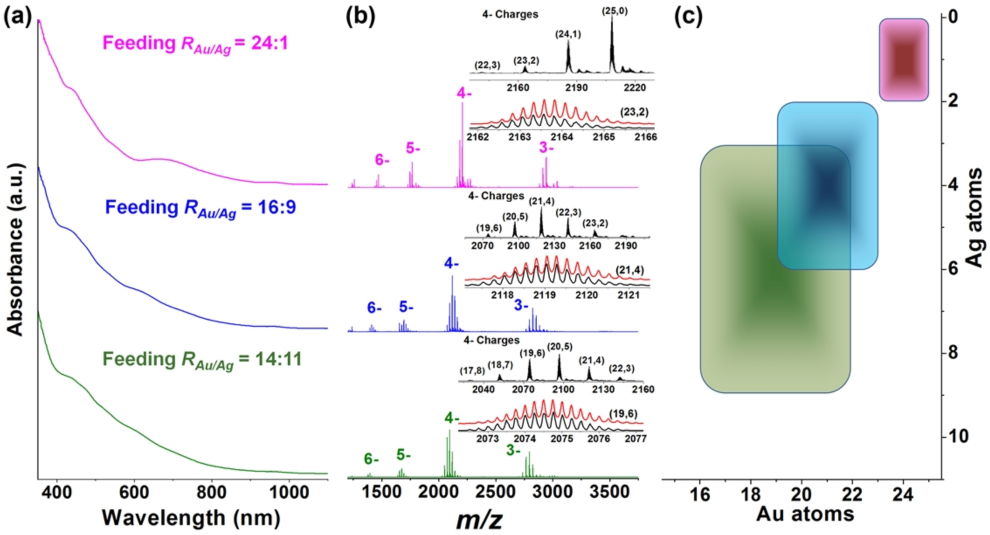

Figure S8. (a) UV-vis absorption spectra, (b) ESI mass spectra, and (c) the compositional distributions of MUA-protected $Au_{25-x}Ag_x$ NCs prepared at different feeding $R_{Au/Ag}$ of 24/1 (pink), 16/9 (blue), and 14/11 (green). Insets in (b) are zoom-in ESI spectra of 4-charged species of the as-synthesized AuAg NCs (upper panel) and representative isotope patterns (lower panel) acquired theoretically (red) and experimentally (black). (c) indicates that the as-synthesized MUA-protected $Au_{25-x}Ag_x$ NCs have different metal compositions: $Au_{23-25}Ag_{2-0}$ NCs ($R_{Au/Ag}$=24/1, pink), $Au_{19-23}Ag_{6-2}$ NCs ($R_{Au/Ag}$=16/9, blue), and $Au_{16-22}Ag_{9-3}$ NCs ($R_{Au/Ag}$=14/11, green).

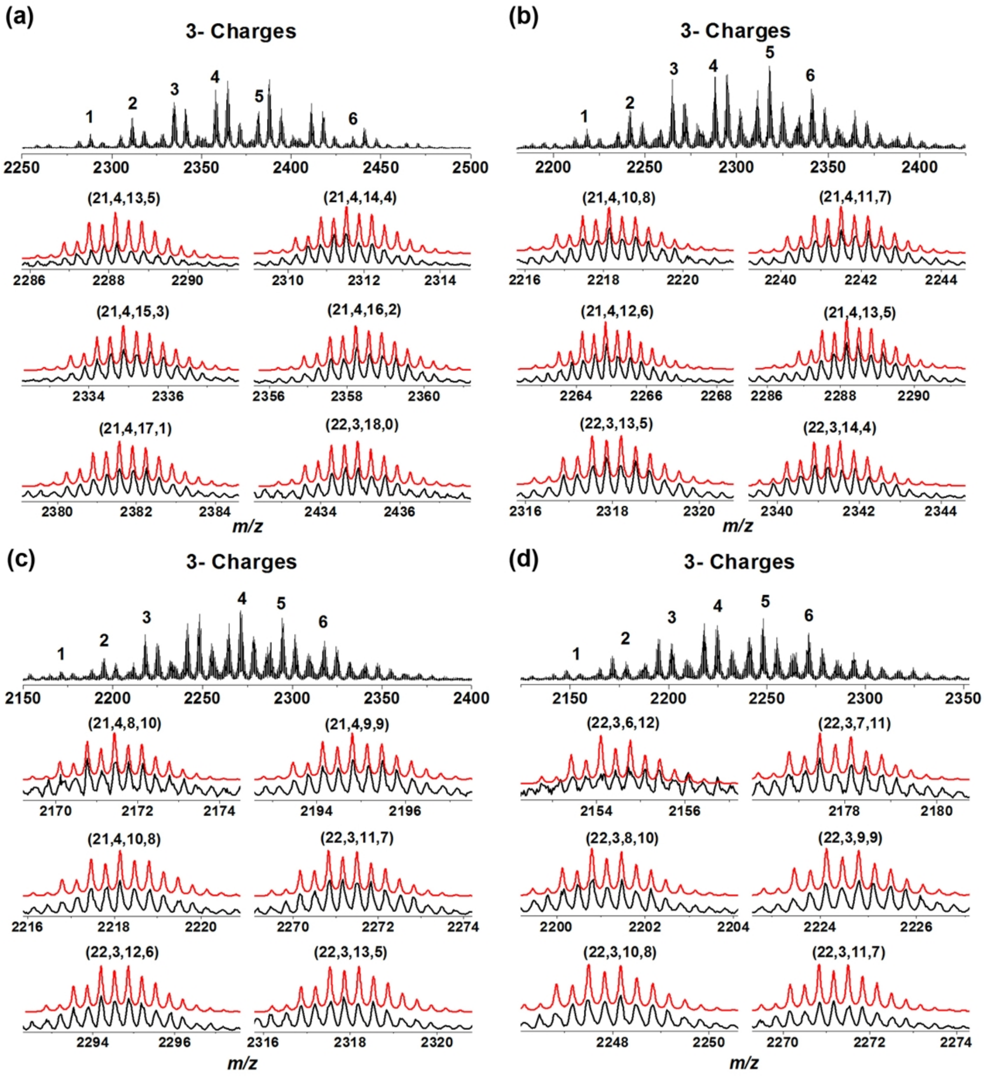

Figure S9. Zoom-in ESI mass spectra and representative isotope patterns (theoretical / red, and experimental / black) of 3- charged MHA/MetH-protected $Au_{25-x}Ag_x$ NCs prepared by keeping the feeding $R_{Au/Ag}$ = 22/3, and varying the feeding $R_{MHA/MetH}$ from (a)1.75/0.25, (b)1.5/0.5, (c)1.25/0.75, to (d) 1.0/1.0. The numbers within the bracket are the number of Au atom, Ag atom, MHA, and MetH in $Au_{25-x}Ag_x(MHA/MetH)_{18}$ NCs. For example, (21, 4, 13, 5) is denoted as $Au_{21}Ag_4(MHA)_{13}(MetH)_5$ NC species.

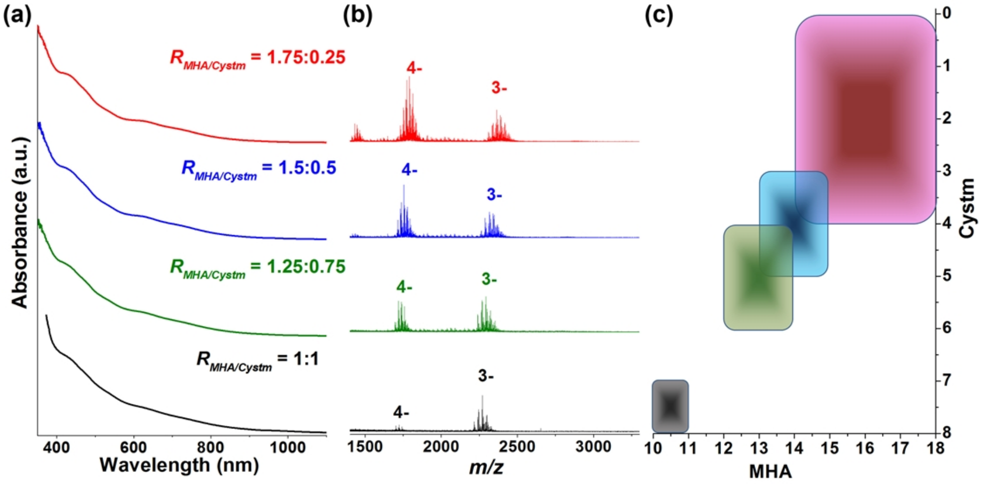

Figure S10. (a) UV-vis absorption, (b) ESI mass spectra, and (c) the hetero-ligand distributions of MHA/Cystm-protected $Au_{25-x}Ag_x$ NCs synthesized by keeping the feeding $R_{Au/Ag}$ = 22/3, and varying the feeding $R_{MHA/Cystm}$ from 1.75/0.25 (red), 1.5/0.5 (blue), 1.25/0.75 (green), to 1.0/1.0 (black). (c) indicates that the as-synthesized MHA/Cystm-protected $Au_{25-x}Ag_x$ NCs have different hetero-ligand distributions: $MHA_{14-18}Cystm_{4-0}$ ($R_{MHA/Cystm}$=1.75/0.25, pink), $MHA_{13-15}Cystm_{5-3}$ ($R_{MHA/Cystm}$=1.5/0.5, blue), $MHA_{12-14}Cystm_{6-4}$ ($R_{MHA/Cystm}$=1.25/0.75, green), and $MHA_{10-11}Cystm_{8-7}$ ($R_{MHA/Cystm}$=1.0/1.0, black).

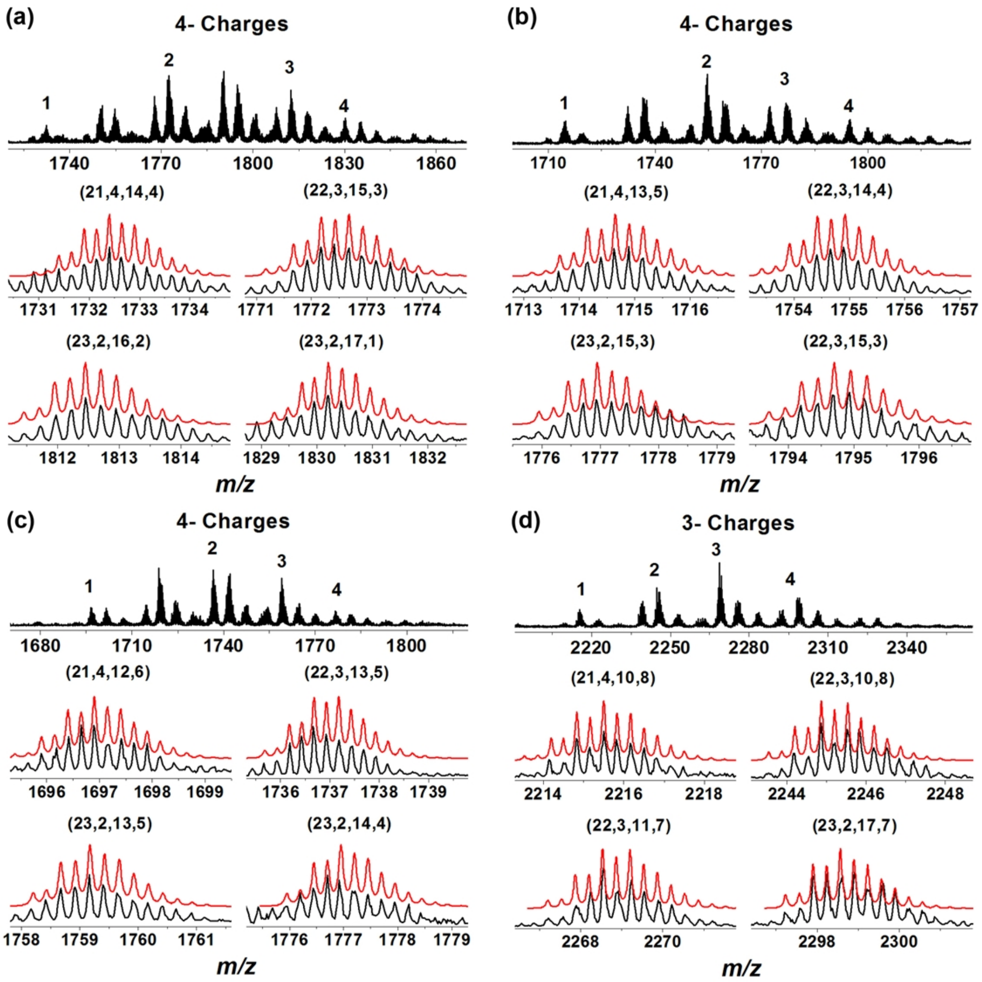

Figure S11. Zoom-in ESI mass spectra and representative isotope patterns (theoretical / red, and experimental / black) of 4- or 3- charged MHA/Cystm-protected $Au_{25-x}Ag_x$ NCs prepared by keeping the feeding $R_{Au/Ag} = 22/3$, and varying the feeding $R_{MHA/MetH}$ from (a) 1.75/0.25, (b) 1.5/0.5, (c) 1.25/0.75, to (d) 1.0/1.0. The numbers within the bracket are the number of Au atom, Ag atom, MHA, and Cystm in $Au_{25-x}Ag_x(MHA/Cystm)_{18}$ NCs. For example, (21, 4, 14, 4) is denoted as $Au_{21}Ag_4(MHA)_{14}(MetH)_4$ NC species.