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Supporting Information

Intrinsically fluorescent gold nanoclusters stabilized within a copper storage protein that follow Irving-Williams trend in metal ion sensing

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DNA sequence of Csp1 with N-terminal Strep-Tag:

TGGAGCCACCCGCAGTTCGAGAAGGGTGGCAGCGGTGAAGACCCGCACGCGGGCCACAAAA
TGAGCCACGGTGCGAAGTACAAAGCGCTGCTGGACAGCAGCAGCCACTGCGTGGCGGTTGG
TGAAGATTGCCTGCGTCACTGCTTTGAAATGCTGGCGATGAACGACGCGAGCATGGGTGCGT
GCACCAAGGCGACCTATGATCTGGTGGCGGCGTGCGGTGCGCTGGCGAAACTGGCGGGTAC
CAACAGCGCGTTCACCCCGGCGTTTGCGAAGGTGGTTGCGGACGTTTGCGCGGCGTGCAAGA
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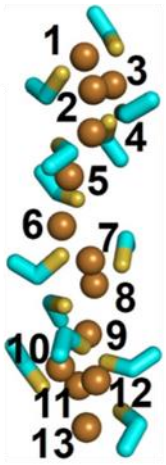

Figure S1. X-ray structure of Cu(I)-Csp1 showing the orientation of all coppers along the protein core.

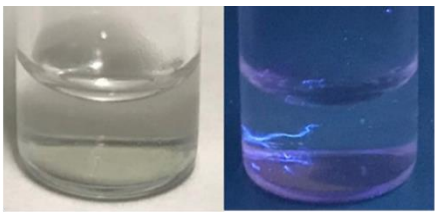

Figure S2. Photographs of the control sample with a variant of Csp1 where all the Cys residues were mutated to non-coordinating Ala and Leu residues. 25 μM of protein was incubated with 150 μM Au^{3+} in the presence of NaOH (4.8% v/v) for 18h at 37°C, under normal light (left); under uv light (right). A lack of luminescence in the absence of thiols indicates that the observed luminesce of the clusters presented in this work is arising from thiol-associated Au at the interior of the protein.

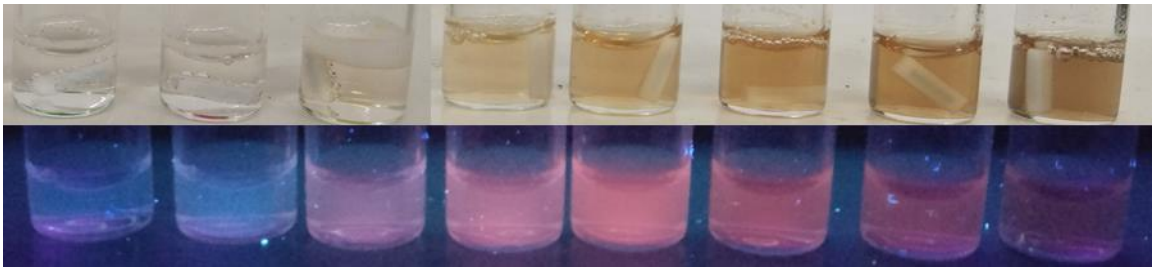

Figure S3. Photographs of AuNC@Csp1 in the presence of 1 to 21 equivalents of Au^{3+} prepared using $NaBH_4$ as reductant, viewed under normal light (top) and uv light (below). Protein concentration was kept constant at 25 μM.

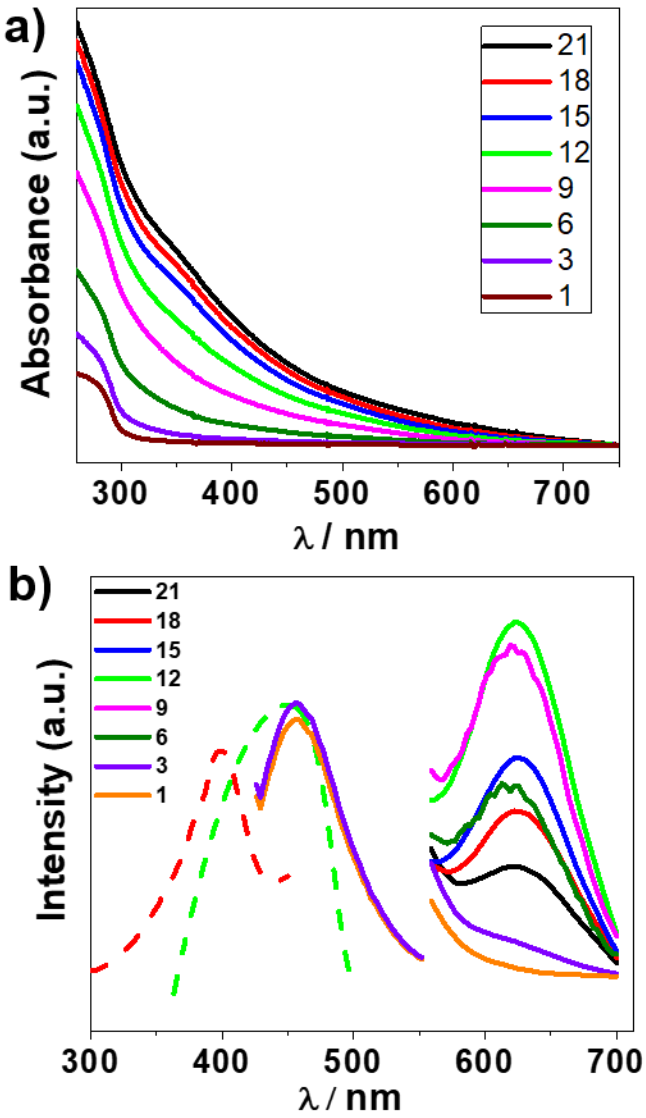

Figure S4. a) UV-vis spectra of AuNC@Csp1 prepared using $NaBH_4$ in the presence of 1-21 equivalents of Au^{3+}. b) Representative photoexcitation and photoemission spectra of the $NaBH_4$ reduced samples. The excitation spectrum for 1 and 3 equivalent Au^{3+} samples is shown as dotted red, while the corresponding emissions are shown in orange/purple in the 450 nm region. The excitation for the 12 equivalent Au^{3+} samples is in dotted green, and the corresponding emission spectra are shown with maxima ~622 nm. The figure legend represents the equivalents of Au^{3+} with respect to protein.

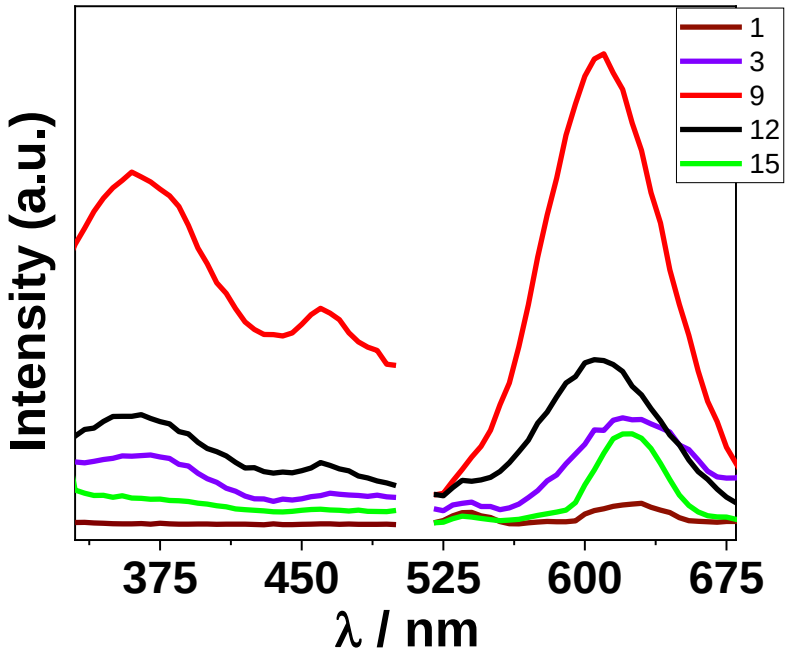

Figure S5. Photoexcitation and photoemission spectra of selected samples prepared by the endogenous reduction method. The figure legend represents the equivalents of Au^{3+} with respect to Csp1.

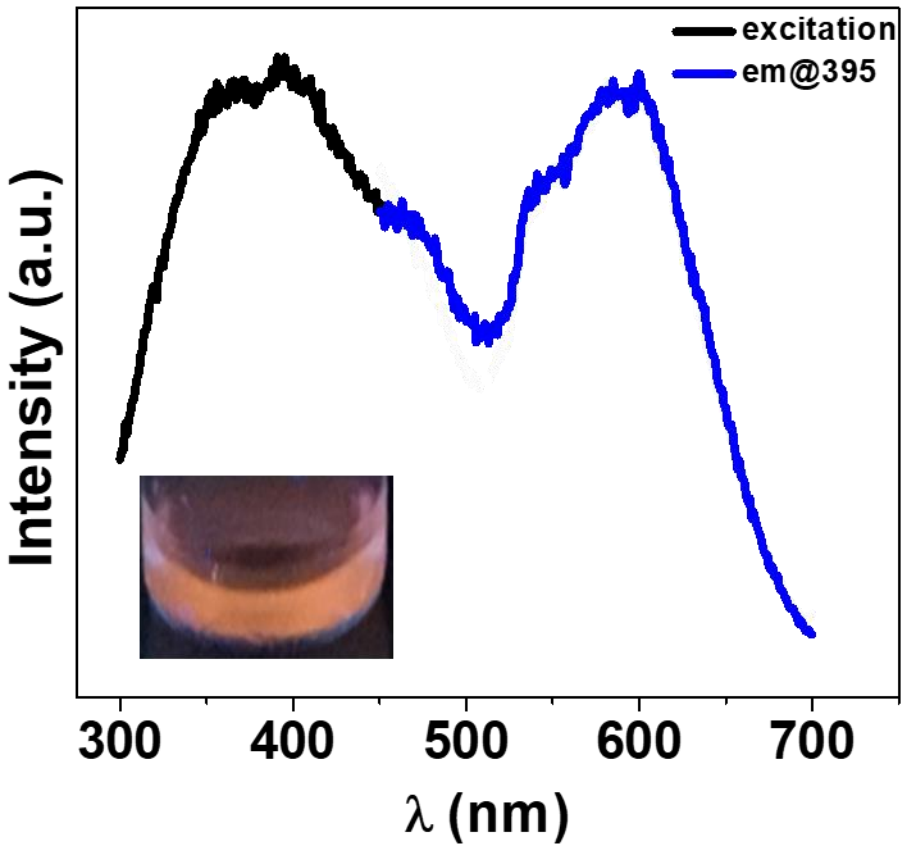

Figure S6. Photoexcitation and photoemission spectra of 9 equivalent Au sample reduced with 15% NaOH (v/v), along with a photograph showing the orange color under UV light (inset).

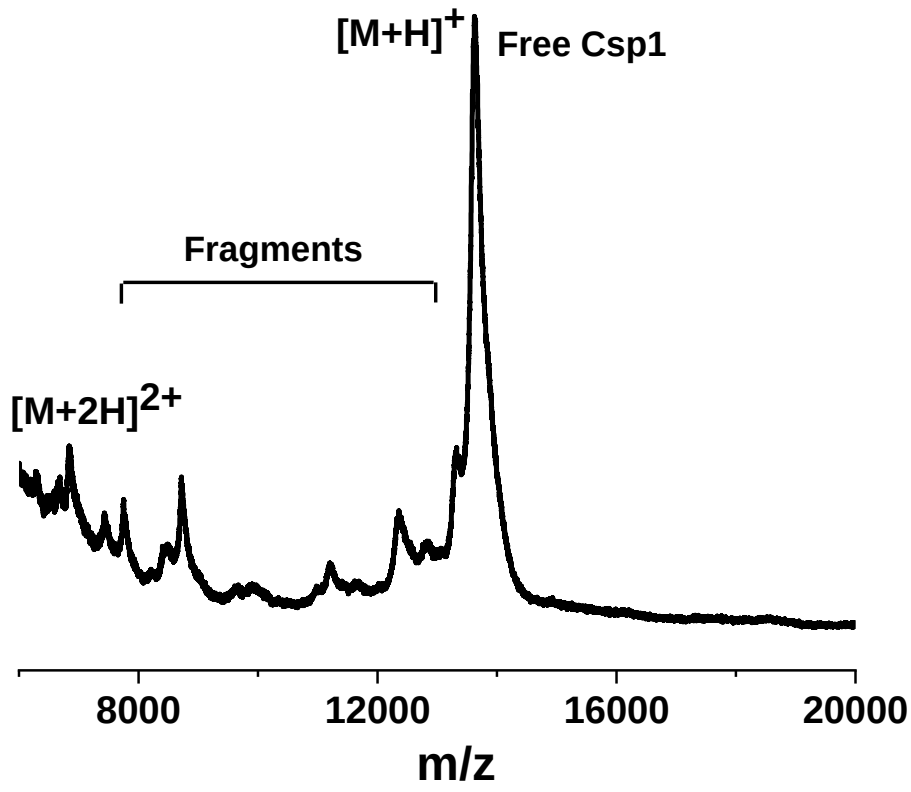

Figure S7. MALDI-MS spectrum of AuNC@Csp1_a in CHCA matrix.

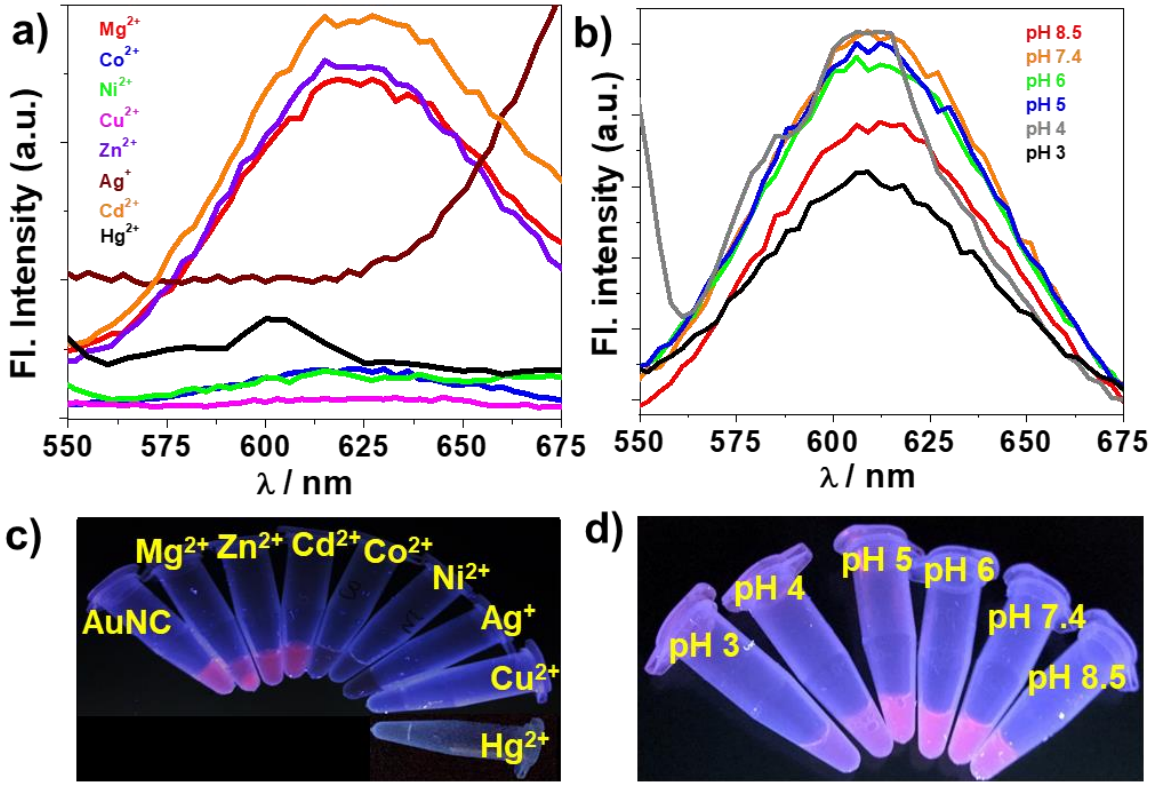

Figure S8. Emission spectra of AuNC@Csp1_a containing 30 ppm Au after incubation with 10-fold excess metal ions for 10 minutes excited at 365 nm (a). The pH-dependent emission spectra of AuNC@Csp1_a are shown in (b). Photographs of the corresponding samples under UV light are shown in (c) and (d), respectively.

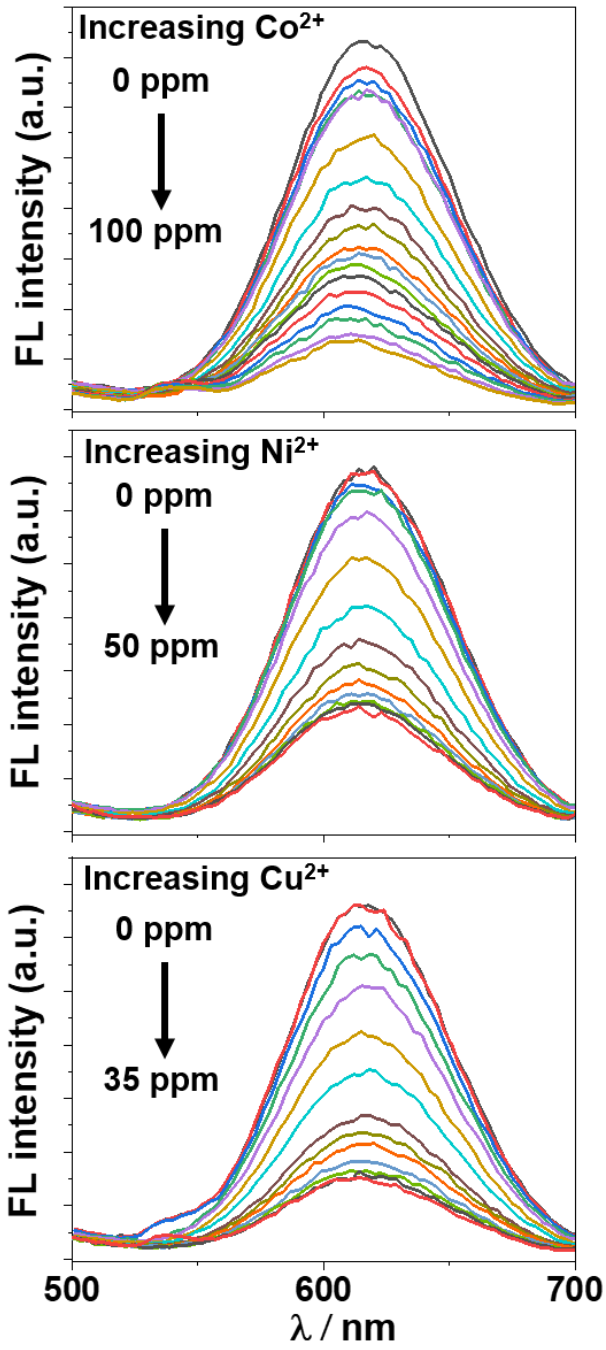

Figure S9. Emission spectra of AuNC@Csp1_a containing 30 ppm Au with increasing concentrations of Co^{2+}, Ni^{2+} and Cu^{2+} excited at 365 nm.

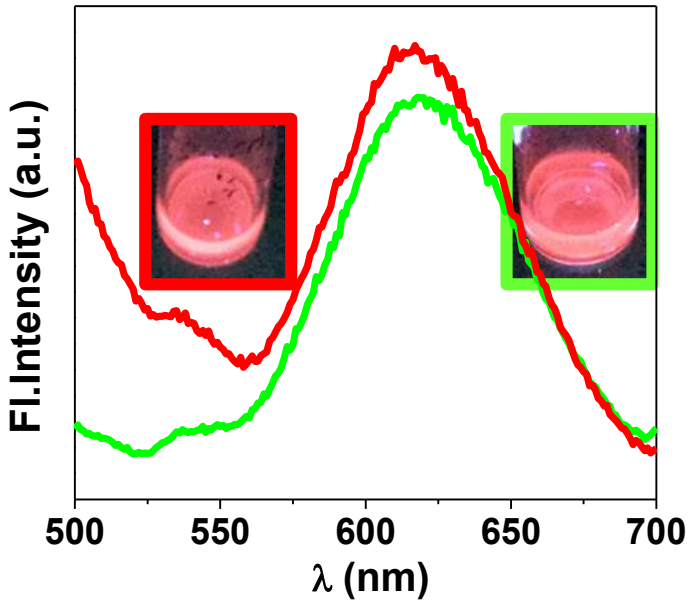

Figure S10. Emission spectra and photographs of a representative cluster sample freshly synthesized (red) and after 4 months (green) demonstrating shelf stability of the clusters over time. Insets show the photographs of these samples under UV light.