## **Electronic Supplementary Information (ESI<sup>†</sup>)**

## **Distinct metal-exchange pathways of doped Ag<sub>25</sub> nanoclusters**

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**Fig. S1** Photographs of  $[PdAg_{24}(SR)_{18}]^{2-}$  and its Au-doped product that containing a predominant product of  $[AuAg_{24}(SR)_{18}]^{-}$  along with a minor product of  $[Au_2Ag_{23}(SR)_{18}]^{-}$  in DCM. Left bottle contains dilute solution of  $[PdAg_{24}(SR)_{18}]^{2-}$  which is orange.



**Fig. S2** Comparison of simulated and experimental mass spectra of (A)  $[AuAg_{24}(SR)_{18}]^-$  and (B)  $[Au_2Ag_{23}(SR)_{18}]^-$  NCs, which are obtained by gold doping of  $[PdAg_{24}(SR)_{18}]^{2-}$  NCs. Note: experimental spectra were shifted by -0.12 amu to match with the simulated ones.



**Fig. S3** Time-dependent ESI MS of gold-doping of  $[PdAg_{24}(SR)_{18}]^{2-}$  NCs. Peaks labeled with "\$" sign are due to unidentified artifacts from the mass spectrometer.



**Fig. S4** (A) SEM image of the Au-doped  $[PdAg_{24}(SR)_{18}]^{2-}$  NCs i.e.,  $[AuAg_{24}(SR)_{18}]^{-}$ + $[Au_2Ag_{23}(SR)_{18}]^{-}$  NCs. (B) EDS spectrum collected from whole region of A, indicating the absence of Pd and the presence of Au in the Au-doped product. The less intense signal of Au is due to the presence of only one or two Au atoms per cluster, in which former is predominant, while the latter is minor. Nevertheless, the presence of Au confirms the successful gold doping. Si is from substrate and P is due to PPh<sub>4</sub>Br.



**Fig. S5** Photographs of DCM solutions of  $[PtAg_{24}(SR)_{18}]^{2-}$  and its Au-doped cluster  $[Au_xPtAg_{24-x}(SR)_{18}]^{2-}$ , x=0-2.



**Fig. S6** (A) SEM image of the Au-doped  $[PtAg_{24}(SR)_{18}]^{2-}$  NCs i.e.,  $[Au_xPtAg_{24-x}(SR)_{18}]^{2-}$  NCs, x=0-2. (B) EDS spectrum collected from the whole region of A, which shows the presence of Pt, Au, S and Ag from Au-doped  $[PtAg_{24}(SR)_{18}]^{2-}$ . The presence of Au confirms the successful gold-doping of  $[PtAg_{24}(SR)_{18}]^{2-}$  NCs and the presence of Pt suggests the intact of Pt after gold-doping.