Supporting information for:

Intercluster Reactions Resulting in Silver-Rich Trimetallic Nanoclusters

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Table of Contents

<table>
<thead>
<tr>
<th>List of figures</th>
<th>Description</th>
<th>Page number</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>UV-vis absorption spectra and ESI MS of Ag$<em>{25}$ and MAg$</em>{24}$ where ‘M’ is Ni, Pd or Pt</td>
<td>3-4</td>
</tr>
<tr>
<td>S2</td>
<td>XPS spectrum of NiAg$<em>{28}$ and time-dependent absorption spectra of NiAg$</em>{24}$, NiAg$<em>{28}$ and Ag$</em>{29}$</td>
<td>4-5</td>
</tr>
<tr>
<td>S3</td>
<td>ESI MS of PdAg$_{28}$ measured under low voltage and low gas pressure conditions</td>
<td>5</td>
</tr>
<tr>
<td>S4</td>
<td>XPS and SEM/EDS spectra of PdAg$_{28}$</td>
<td>6</td>
</tr>
<tr>
<td>S5</td>
<td>UV-vis absorption spectrum and ESI MS of PtAg$_{28}$</td>
<td>7</td>
</tr>
<tr>
<td>S6</td>
<td>The collision-induced dissociation mass spectra of [NiAg(<em>{28}(\text{BDT})</em>{12})](^+) and [PdAg(<em>{28}(\text{BDT})</em>{12})](^+)</td>
<td>8</td>
</tr>
<tr>
<td>S7</td>
<td>Theoretical structures of various isomers of NiAg(<em>{28}) and PdAg(</em>{28})</td>
<td>9-10</td>
</tr>
<tr>
<td>S8</td>
<td>Concentration-dependent ESI MS of the reaction between PdAg(<em>{28}) and Au(</em>{25})</td>
<td>11</td>
</tr>
<tr>
<td>S9</td>
<td>Theoretical and experimental isotopic distributions of PdAu(<em>{12})Ag(</em>{16})</td>
<td>11</td>
</tr>
<tr>
<td>S10</td>
<td>Time-dependent UV-vis absorption spectra of intercluster reaction between PdAg(<em>{28}) and Au(</em>{25})</td>
<td>12</td>
</tr>
<tr>
<td>S11</td>
<td>Theoretical and experimental isotopic distributions of PtAu(<em>{12})Ag(</em>{16})</td>
<td>12</td>
</tr>
<tr>
<td>S12</td>
<td>Time-dependent ESI MS of intercluster reaction between PtAg(<em>{28}) and Au(</em>{25}) showing the reaction at Au(_{25})</td>
<td>13</td>
</tr>
<tr>
<td>S13</td>
<td>Time-dependent UV-vis absorption spectra of intercluster reaction between PtAg(<em>{28}) and Au(</em>{25})</td>
<td>13</td>
</tr>
<tr>
<td>S14</td>
<td>Time-dependent ESI MS of NiAg(_{28}) which show the formation of trimetallic NiAu(<em>x)Ag(</em>{28-x})</td>
<td>14</td>
</tr>
<tr>
<td>S15</td>
<td>Experimental and theoretical isotopic patterns of NiAu(<em>{12})Ag(</em>{16})</td>
<td>14</td>
</tr>
<tr>
<td>S16</td>
<td>Concentration-dependent ESI MS of the reaction between Ag(<em>{29}) and Au(</em>{25})</td>
<td>15</td>
</tr>
<tr>
<td>S17</td>
<td>Time-dependent absorption spectra of the reaction between Ag(<em>{29}) and Au(</em>{25}) at room temperature</td>
<td>15</td>
</tr>
<tr>
<td>S18</td>
<td>Experimental and theoretical isotopic patterns of Au(<em>{12})Ag(</em>{17})</td>
<td>16</td>
</tr>
<tr>
<td>S19</td>
<td>Time-dependent ESI MS of the reaction between Ag(<em>{29}) and Au(</em>{25}) at Au(_{25}) side (higher temperature)</td>
<td>16</td>
</tr>
<tr>
<td>S20</td>
<td>Time-dependent UV-vis absorption spectra of the intercluster reaction between Ag(<em>{29}) and Au(</em>{25})</td>
<td>17</td>
</tr>
</tbody>
</table>
Three different DFT optimized geometric isomers of Au$_{12}$Ag$_{17}$ and their energies.

Supporting information 1:

A) a) $\text{Ag}_{25}(\text{DMBT})_{18}$

b) $\text{Ag}_{24}\text{Ni}(\text{DMBT})_{18}$

c) $\text{Ag}_{24}\text{Pd}(\text{DMBT})_{18}$

d) $\text{Ag}_{24}\text{Pt}(\text{DMBT})_{18}$

B) a') $[\text{Ag}_{25}(\text{DMBT})_{18}]^-$

m/z 5167

b') $[\text{Ag}_{24}\text{Ni}(\text{DMBT})_{18}]^{2-}$

m/z 2558

c') $[\text{Ag}_{24}\text{Pd}(\text{DMBT})_{18}]^{2-}$

m/z 2581

d') $[\text{Ag}_{24}\text{Pt}(\text{DMBT})_{18}]^{2-}$

m/z 2626
**Figure S1.** (A) UV-vis absorption spectra and (B) ESI MS of Ag$_{25}$ (panel a/a’) and MAg$_{24}$ where ‘M’ is Ni, Pd and Pt (panel b/b’, c/c’ and d/d’). Upon doping of Ni, Pd and Pt in Ag$_{25}$, absorption features show gradual blue-shifts. (C) Time-dependent absorption spectra of (a) Ag$_{25}$ and (b) NiAg$_{24}$ which were kept at room temperature.

**Supporting information 2:**
Figure S2. (A) XPS spectrum of NiAg\textsubscript{28} shows the presence of Ni 2p, Ag 3d, P 2p and S 2p. (B) Time-dependent absorption spectra of (a) NiAg\textsubscript{24} and (b) NiAg\textsubscript{28} at room temperature. (C) Time-dependent absorption spectra of (a) Ag\textsubscript{29} and (b) NiAg\textsubscript{28} at 60°C temperature.

Supporting information 3:
Figure S3. ESI MS of PdAg$_{28}$ measured under low voltage and low gas pressure conditions shows the presence of four PPh$_3$ ligands.

Supporting information 4:

Figure S4. (A) XPS spectrum of PdAg$_{28}$ shows the presence of Pd, Ag, P and S. Pd 3d$_{5/2}$ peak arises at 337.5 eV which is higher than that of Pd (0) (335.5 eV) and Ag 3d$_{5/2}$ peak arises at 368.5 eV which is also at a higher value than that of Ag (0) (367.9 eV) which manifest a partial charge transfer from Pd to Ag. (B) SEM image of PdAg$_{28}$ and EDS mapping of C, P, S, Ag and Pd.
Supporting information 5:

Figure S5. (A) UV-vis absorption spectrum of PtAg$_{28}$ which possesses two prominent features at 425 and 491 nm. The absorption peaks are 22 nm blue-shifted from that of Ag$_{29}$. (B) ESI MS of PtAg$_{28}$ exhibits two intense peaks at m/z 1224 and 1632 which correspond to [PtAg$_{28}$(BDT)$_{12}$]$^{4-}$ and [PtAg$_{28}$(BDT)$_{12}$]$^{3-}$, respectively. Theoretical and experimental isotopic distributions of [PtAg$_{28}$(BDT)$_{12}$]$^{4-}$ are shown in the inset of (B) which are well fitted.
Supporting information 6:

Figure S6. The collision-induced dissociation mass spectra of (A) [NiAg_{28}(BDT)_{12}]^{+} (m/z 1190) and (B) [PdAg_{28}(BDT)_{12}]^{+} (m/z 1202).
Supporting information 7:

A)  

a)  

\[ E = -1812.76 \text{ eV} \]  

b)  

\[ E = -1812.95 \text{ eV} \]  

c)  

\[ E = -1812.68 \text{ eV} \]  

A)  

Ag S P Ni
Figure S7. Theoretical structures of different isomers of (A) NiAg$_{28}$ and (B) PdAg$_{28}$. Mainly four isomers of NiAg$_{28}$ and PdAg$_{28}$ were observed and three of them are shown here; (a) Ni/Pd atom is doped in the icosahedral surface, (b) Ni/Pd atom is doped in crown staples and (c) Ni/Pd atom replaces Ag atom which is bonded to PPh$_3$. 

$E = -1810.86$ eV $E = -1810.28$ eV $E = -1810.85$ eV
Supporting information 8:

**Figure S8.** Concentration-dependent ESI MS of the reaction between PdAg_{28} and Au_{25} using 4:1, 2:1, 1:1, 1:2 and 1:5 molar ratios at three different time intervals, (A) 1 h, (B) 6 h and (C) 24 h.

Supporting information 9:

**Figure S9.** The experimental isotopic distribution (black trace) of PdAu_{12}Ag_{16} which matches exactly with the theoretical one (red trace).
Supporting information 10:

**Figure S10.** Time-dependent UV-vis absorption spectra of intercluster reaction between PdAg$_{28}$ and Au$_{25}$ using a 1:5 molar ratio.

Supporting information 11:

**Figure S11.** The experimental isotopic distribution (blue trace) of PtAu$_{12}$Ag$_{16}$ which matches exactly with the theoretical one (red trace).
Supporting information 12:

**Figure 12.** Time-dependent ESI MS of intercluster reaction between PtAg₂₈ and Au₂₅ (1:5 molar ratio) showing the reaction at Au₂₅ side which show formation of AgₓAu₂₅₋ₓ (x= 0-7).

Supporting information 13:

**Figure S13.** Time-dependent UV-vis absorption spectra of intercluster reaction between PtAg₂₈ and Au₂₅ using a 1:5 molar ratio.
Supporting information 14:

Figure S14. Time-dependent ESI MS of intercluster reaction between NiAg$_{28}$ and Au$_{25}$ using a 1:5 molar ratio which show the formation of trimetallic NiAu$_{x}$Ag$_{28-x}$.

Supporting information 15:

Figure S15. Experimental and theoretical isotopic patterns (green trace) of NiAuAg$_{27}$ (red trace) fit well with each other.
Supporting information 16:

Figure S16. Concentration-dependent ESI MS of the reaction between Ag_{29} and Au_{25} using 1:1, 1:5 and 1:10 molar ratios at 6h which lead to the formation of Au_{x}Ag_{29-x} (x = 1-8).

Supporting information 17:
Figure S17. Time-dependent absorption spectra of the reaction between Ag$_{29}$ and Au$_{25}$ (1:5 ratio) at room temperature resulting in the formation of Au$_{x}$Ag$_{29-x}$ ($x = 1$-12).

Supporting information 18:

![Figure S18. Experimental and theoretical isotopic patterns of Au$_{12}$Ag$_{17}$ which shows good agreement with each other.](image)

Supporting information 19:

![Figure S19. Experimental and theoretical isotopic patterns of Au$_{x}$Ag$_{25-x}$](image)
Figure S19. Time-dependent ESI MS of the reaction between Ag$_{29}$ and Au$_{25}$ (1:5 ratio) at the Au$_{25}$ side (higher temperature).

Supporting information 20:

![Graph showing time-dependent UV-vis absorption spectra of the reaction](image)

Figure S20. Time-dependent UV-vis absorption spectra of the intercluster reaction between Ag$_{29}$ and Au$_{25}$ using a 1:5 molar ratio.

Supporting information 21:
**Figure S21.** Three different geometric isomers of $\text{Au}_{12}\text{Ag}_{17}$; (a) 12 Au atoms are doped in the icosahedral surface, (b) among 12 Au atoms, 8 Au atoms are doped in the crown staples and remaining 4 Au atoms are doped in Ag-PPh$_3$ motifs and (c) 12 Au atoms are doped in the crown motifs.