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# DFT Studies on the Influence of ligation in optical and redox properties of bimetallic $[Au_4M_2]$ clusters

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Table S1. Computed vibrational frequencies for M-M, M-S and M-P bonds of bare $[Au_4M_2]$, $[Au_4M_2(SCH_3)_6]$ and $[Au_4M_2(PH_3)_6]^{2+}$, M=Au, Cu, Ag, Ni, Pd and Pt clusters using CAM-B3LYP functional are given in ($cm^{-1}$).

| Clusters | Bare $[Au_4M_2]$ | | $[Au_4M_2(SCH_3)_6]$ | | | $[Au_4M_2(PH_3)_6]^{+2}$ | | |
|---|---|---|---|---|---|---|---|---|
| | Au-Au | M-M | M-S | M-M | Au-Au | M-P | M-M | Au-Au |
| M=Au | 32-120 | 32-120 | 312-342 | 13-54 | 13-54 | 60-243 | 33-133 | 33-133 |
| M=Cu | 38-162 | 38-260 | 184-368 | 11-67 | 11-46 | 50-270 | 40-200 | 42-133 |
| M=Ag | 27-187 | 27-192 | 291-346 | 10-64 | 10-70 | 48-248 | 62-153 | 49-153 |
| M=Ni | 28-169 | 43-226 | 197-369 | 15-75 | 15-75 | 163-343 | 73-162 | 54-233 |
| M=Pd | 32-200 | 32-221 | 205-358 | 9-81 | 23-74 | 141-293 | 61-172 | 52-163 |
| M=Pt | 15-206 | 33-206 | 196-368 | 16-57 | 16-105 | 136-338 | 76-160 | 56-160 |

Table S2. Structural Parameters (Å) of bare $[Au_4M_2]$ where M=Au, Cu, Ag, Ni, Pd and Pt clusters computed using CAM-B3LYP functional. Calculated Height (average distance between the Au-M and M-Au atoms in outer triangle), Breadth (average distance between the Au-Au and Au-Au in outer triangle) are given. And reported values given in *italics*.[1,2,3,4,6]

| Clusters $[Au_4M_2]$ | Au-M | M-M | Au-M-M | M-Au-M' | Height | Breadth |
|---|---|---|---|---|---|---|
| M=Au | 2.678<br>*2.704* | 2.867<br>*2.903* | 57.69 | 64.69 | 5.35 | 5.35 |
| M=Cu | 2.523 | 2.606 | 58.60 | 62.80 | 5.04 | 5.28 |
| M=Ag | 2.705<br>*2.703* | 2.922 | 57.19 | 65.61 | 5.41 | 5.30 |
| M=Ni | 2.525<br>*2.270* | 2.213 | 63.40 | 53.19 | 5.03 | 5.26 |
| M=Pd | 2.725<br>*2.640* | 2.651 | 60.46 | 59.21 | 5.28 | 5.28 |
| M=Pt | 2.643<br>*2.640* | 4.496 | 61.58 | 56.81 | 5.28 | 5.30 |

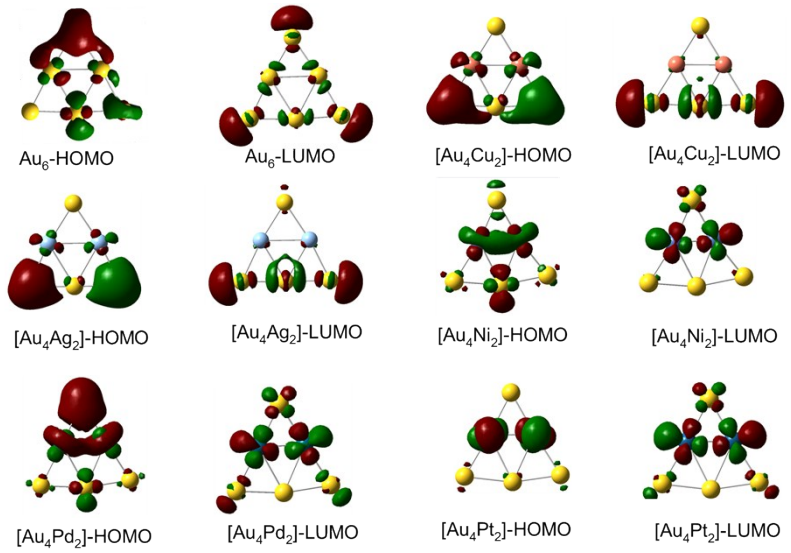



Figure S1. Computed HOMO and LUMO of bare $[Au_4M_2]$ BMGC, where M= Au, Cu, Ag, Ni, Pd and Pt (orbitals are plotted with isocontour value: 0.04 $Å^{-3}$).

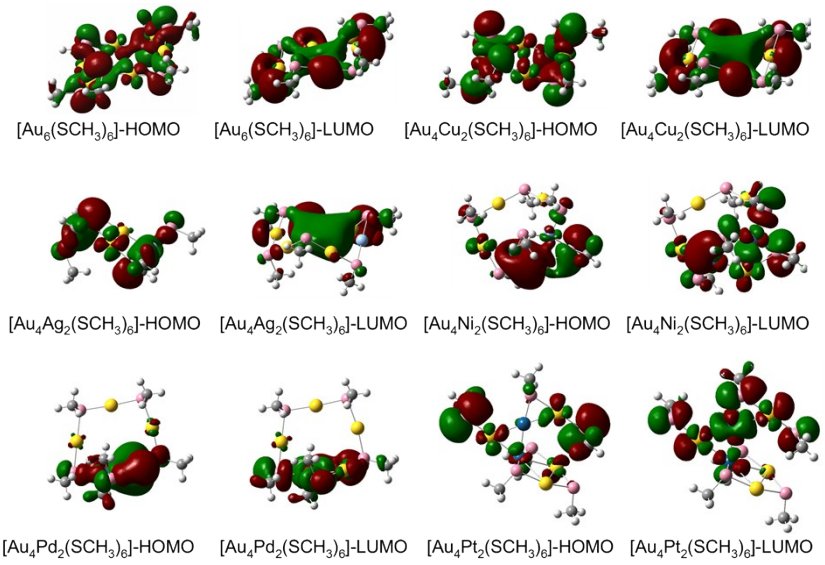



Figure S2. Computed HOMO and LUMO of ligated $[Au_4M_2(SCH_3)_6]$ BMGC, where M= Au, Cu, Ag, Ni, Pd and Pt (orbitals are plotted with isocontour value: 0.04 $Å^{-3}$).

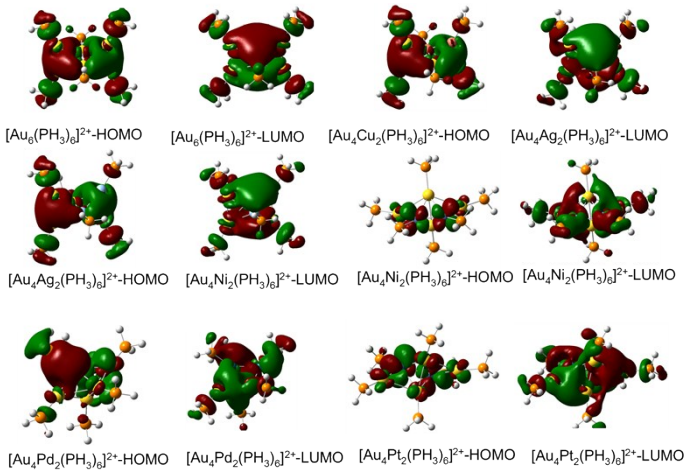



Figure S3. Computed HOMO and LUMO of ligated $[Au_4M_2(PH_3)_6]$ BMGC, where M= Au, Cu, Ag, Ni, Pd and Pt (orbitals are plotted with isocontour value: 0.04 $Å^{-3}$).

Table S3. Computed redox properties of bare $[Au_4M_2]$ where M=Au, Cu, Ag, Ni, Pd and Pt clusters using Polarizable Continuum Model (PCM) in Water, DMSO and DCM. Calculated AIP, AEA, $\Delta=E_{LUMO}-E_{HOMO}$ are given in (eV).

| Cluster | Media | AIP | AEA | Δ |
|---|---|---|---|---|
| $Au_6$ | Water | 5.84 | 2.65 | 5.89 |
| | DMSO | 5.86 | 2.63 | 5.95 |
| | DCM | 6.08 | 2.49 | 5.90 |
| $Au_4Cu_2$ | Water | 5.84 | 3.06 | 5.85 |
| | DMSO | 5.92 | 3.08 | 5.91 |
| | DCM | 6.16 | 1.97 | 5.86 |
| $Au_4Ag_2$ | Water | 5.03 | 2.90 | 5.79 |
| | DMSO | 5.11 | 2.92 | 5.85 |
| | DCM | 5.38 | 2.81 | 5.82 |
| $Au_4Ni_2$ | Water | 3.07 | 4.32 | 5.32 |
| | DMSO | 3.12 | 4.21 | 5.38 |
| | DCM | 2.80 | 4.08 | 5.35 |
| $Au_4Pd_2$ | Water | 4.55 | 4.72 | 3.98 |
| | DMSO | 4.62 | 4.76 | 4.02 |
| | DCM | 4.92 | 4.66 | 3.96 |
| $Au_4Pt_2$ | Water | 4.64 | 3.90 | 4.71 |
| | DMSO | 4.67 | 3.94 | 4.76 |
| | DCM | 4.87 | 3.87 | 4.73 |

Table S4. Structural Parameters, bond length (Å), bond angle (°) of ligated $[Au_4M_2(L)_6]^n$ where n=0 for L=$SCH_3$ and n=+2 for L=$PH_3$, M=Au, Cu, Ag, Ni, Pd and Pt clusters computed using CAM-B3LYP functional. And reported values are given in *italics*.[5]

| Clusters $[Au_4M_2(L)_6]^n$ | Au-L | | M-L | | L-Au-L | | L-M-L | | M-M | | M-M-L | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | L=S | L=P | L=S | L=P | L=S | L=P | L=S | L=P | L=S | L=P | L=S | L=P |
| M=Au | 2.360<br>*2.380* | 2.404 | 2.360 | 2.402 | 179 | - | 179 | - | - | 2.708 | - | 139 |
| M=Cu | 2.356 | 2.422 | 2.226 | 2.336 | 179 | - | 177 | - | - | 2.702 | - | 140 |
| M=Ag | 2.359 | 2.422 | 2.440 | 2.543 | 178 | - | 178 | - | - | 3.069 | - | 138 |
| M=Ni | 2.201 | 2.390 | 2.238 | 2.191 | 178 | - | 100 | - | 3.203 | 2.301 | 142 | 132 |
| M=Pd | 2.363 | 2.347 | 2.413 | 2.307 | 171 | - | 154 | - | 2.824 | 2.801 | 145 | 133 |
| M=Pt | 2.376 | 2.339 | 2.279 | 2.266 | 176 | - | 163 | - | 2.602 | 2.689 | 172 | 134 |

Table S5. Computed natural charge (e) values for ligated $[Au_4M_2(SCH_3)_6]$ and $[Au_4M_2(PH_3)_6]^{2+}$ where M=Au, Cu, Ag, Ni, Pd and Pt clusters using CAM-B3LYP functional.

| Clusters | $[Au_4M_2(SCH_3)_6]$ | | | $[Au_4M_2(PH_3)_6]^{+2}$ | | |
|---|---|---|---|---|---|---|
| | Au | M | S | Au | M | P |
| M=Au | -0.28 | -0.28 | 0.22 | 0.11 | -0.16 | 0.10 |
| M=Cu | -0.24 | 0.45 | 0.30 | 0.08 | 0.11 | 0.06 |
| M=Ag | -0.25 | 0.51 | 0.31 | 0.05 | 0.20 | 0.06 |
| M=Ni | -0.30 | 0.04 | 0.10 | 0.17 | -0.19 | 0.12 |
| M=Pd | -0.32 | 0.04 | 0.24 | 0.20 | -0.26 | 0.13 |
| M=Pt | -0.33 | 0.05 | 0.20 | 0.22 | -0.48 | 0.20 |

Table S6. Computed redox properties of ligated $[Au_4M_2(L)_6]^{+n}$, M=Au, Cu, Ag, Ni, Pd and Pt clusters using Polarizable Continuum Model(PCM) in Water, DMSO and DCM. Calculated AIP, AEA, $\Delta=E_{LUMO}-E_{HOMO}$ are given in (eV).

| Clusters | Media | $[Au_4M_2(SCH_3)_6]$ | | | $[Au_4M_2(PH_3)_6]^{+2}$ | | |
|---|---|---|---|---|---|---|---|
| | | AIP | AEA | Δ | AIP | AEA | Δ |
| M=Au | Water | 6.30 | 1.83 | 7.82 | 6.00 | 3.00 | 3.65 |
| | DMSO | 6.35 | 1.81 | 7.82 | 6.13 | 3.06 | 3.69 |
| | DCM | 6.53 | 1.61 | 7.81 | 6.82 | 3.39 | 3.68 |
| M=Cu | Water | 7.95 | 1.20 | 7.74 | 5.44 | 2.65 | 3.48 |
| | DMSO | 7.97 | 1.19 | 7.73 | 5.57 | 2.71 | 3.39 |
| | DCM | 8.41 | 1.03 | 7.73 | 6.27 | 3.07 | 3.48 |
| M=Ag | Water | 7.32 | 1.54 | 7.88 | 5.19 | 2.49 | 3.44 |
| | DMSO | 7.34 | 1.53 | 7.90 | 5.32 | 2.55 | 3.47 |
| | DCM | 7.52 | 1.39 | 7.91 | 6.04 | 2.91 | 3.44 |
| M=Ni | Water | 745 | 3.50 | 4.77 | 4.43 | 3.58 | 2.80 |
| | DMSO | 7.68 | 2.55 | 4.76 | 4.55 | 3.66 | 2.69 |
| | DCM | 8.93 | 3.28 | 4.74 | 5.33 | 4.03 | 2.71 |
| M=Pd | Water | 4.55 | 3.76 | 4.51 | 5.45 | 3.23 | 3.10 |
| | DMSO | 4.57 | 3.77 | 4.59 | 5.59 | 3.30 | 3.14 |
| | DCM | 4.79 | 3.58 | 4.60 | 6.38 | 3.66 | 3.13 |
| M=Pt | Water | 5.12 | 5.07 | 4.03 | 5.29 | 2.92 | 3.28 |
| | DMSO | 5.83 | 5.06 | 4.38 | 5.43 | 4.37 | 3.38 |
| | DCM | 5.95 | 5.06 | 4.30 | 6.22 | 3.35 | 3.32 |

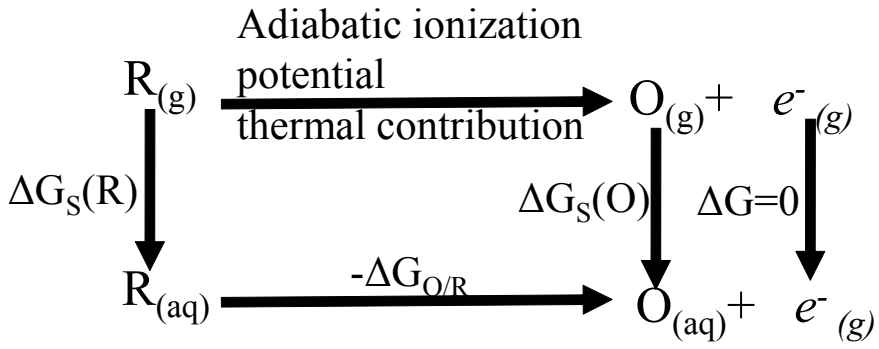
Redox potential calculations

The standard reduction potential calculations were performed in solution (water as solvent) based on thermochemical Born-Haber cycle illustrated in scheme 1 by Cramer and Truhlar.[7] The complete scheme has been splitted into two one electron processes labelled as oxidation (ionization) and reduction (electron affinity) cycles separately.

$$[Au_4M_2L_6]^{n+0} \underset{+e}{\overset{-e}{\rightleftharpoons}} [Au_4M_2L_6]^{n-1} \text{-----Oxidation cycle}$$

$$[Au_4M_2L_6]^{n+0} \underset{-e}{\overset{+e}{\rightleftharpoons}} [Au_4M_2L_6]^{n+1} \text{ -----Reduction Cycle}$$

**Where, n=number of electrons, M= Au, Ag, Cu, Ni, Pt, Pd and L= $SCH_3$ and $PH_3$**




Here, $\Delta G_{AIP(gas)}$ and $\Delta G_{AEA(gas)}$ are the adiabatic free energy changes during the oxidation(ionization)/reduction(electron affinity) of BMGC in the gas phase. And the standard state free energy of solvation are calculated using following equation for oxidised and reduced species,

$$\Delta G_S^{ox1/red1/ox2/red2} = G_{ox1/red1/ox2/red2}^{Solv} - G_{ox1/red1/ox2/red2}^{Gas}$$

$$\Delta\Delta G_{IP} = \Delta G_S^{ox1} - \Delta G_S^{red1}$$

$$\Delta\Delta G_{EA} = \Delta G_S^{red2} - \Delta G_S^{ox2}$$

$$E^o_{IP/EA} = \frac{\Delta\Delta G_{IP/EA} + \Delta\Delta G_{AIP/AEA} + E^o_{SHE}}{nF}$$

Where $E^o_{SHE}$ is the Standard hydrogen electrode redox potential (-4.28) in eV, n is number of electrons and always considered as one and F is a Faraday constant.

Table S7. Computed standard redox potentials (V) for one electron oxidation/reduction processes of bare and ligated bimetallic gold nanoclusters calculated using Born-Haber cycle.

| $[Au_4M_2]$ | $E^o_{IP}$ | $E^o_{EA}$ | $[Au_4M_2(SCH_3)_6]$ | $E^o_{IP}$ | $E^o_{EA}$ | $[Au_4M_2(PH_3)_6]^{+2}$ | $E^o_{IP}$ | $E^o_{EA}$ |
|---|---|---|---|---|---|---|---|---|
| M=Au | 1.38 | -1.71 | M=Au | 2.10 | -2.38 | M=Au | 1.28 | -1.82 |
| M=Cu | 1.43 | -1.15 | M=Cu | 3.61 | -2.10 | M=Cu | 1.25 | -1.75 |
| M=Ag | 1.19 | -1.31 | M=Ag | 3.10 | -2.46 | M=Ag | 1.18 | -1.46 |
| M=Ni | 0.57 | -0.26 | M=Ni | 1.75 | -0.54 | M=Ni | 1.23 | -0.81 |
| M=Pd | 0.27 | -0.54 | M=Pd | 1.06 | -0.81 | M=Pd | 1.30 | -1.15 |
| M=Pt | 0.10 | -0.34 | M=Pt | 1.55 | -0.97 | M=Pt | 1.05 | -1.25 |

**References**

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