Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Ligand removal energetics control CO_2 electroreduction selectivity on atomically precise, ligated alloy nanoclusters

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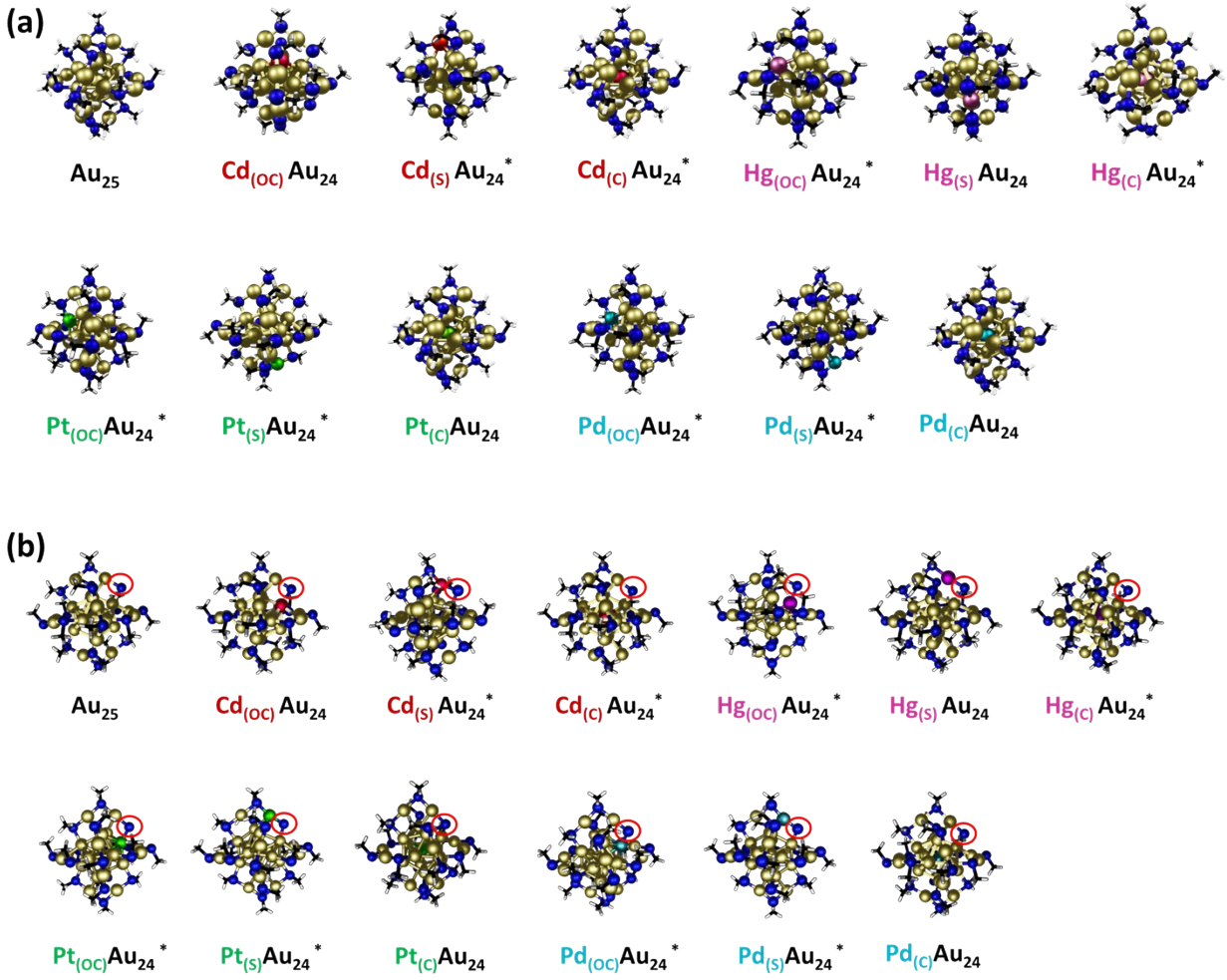

Figure S1. Structures of all optimized TPNCs in their (a) fully protected state and (b) upon -R removal. Dopants indicated by color. Au_{25} has the same optimized structure in the neutral state and the negatively charged state. Hypothetical systems are labeled with *. Red circle indicates site of -R removal.

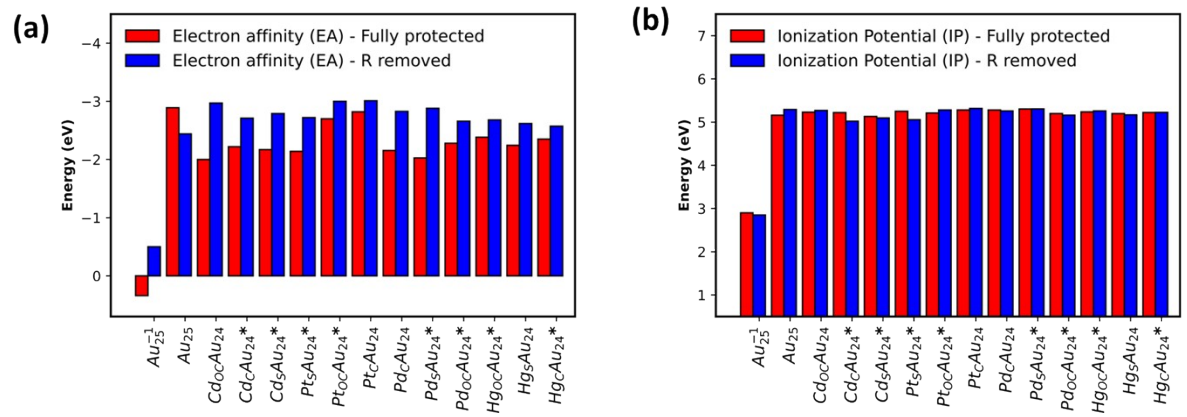

Figure S2. (a) EA and (b) IP of all TPNCs (including Au_{25} in its negative (-1) charge state) in their fully protected state (red bars) and upon -R removal (blue bars). Hypothetical systems are labeled with *.

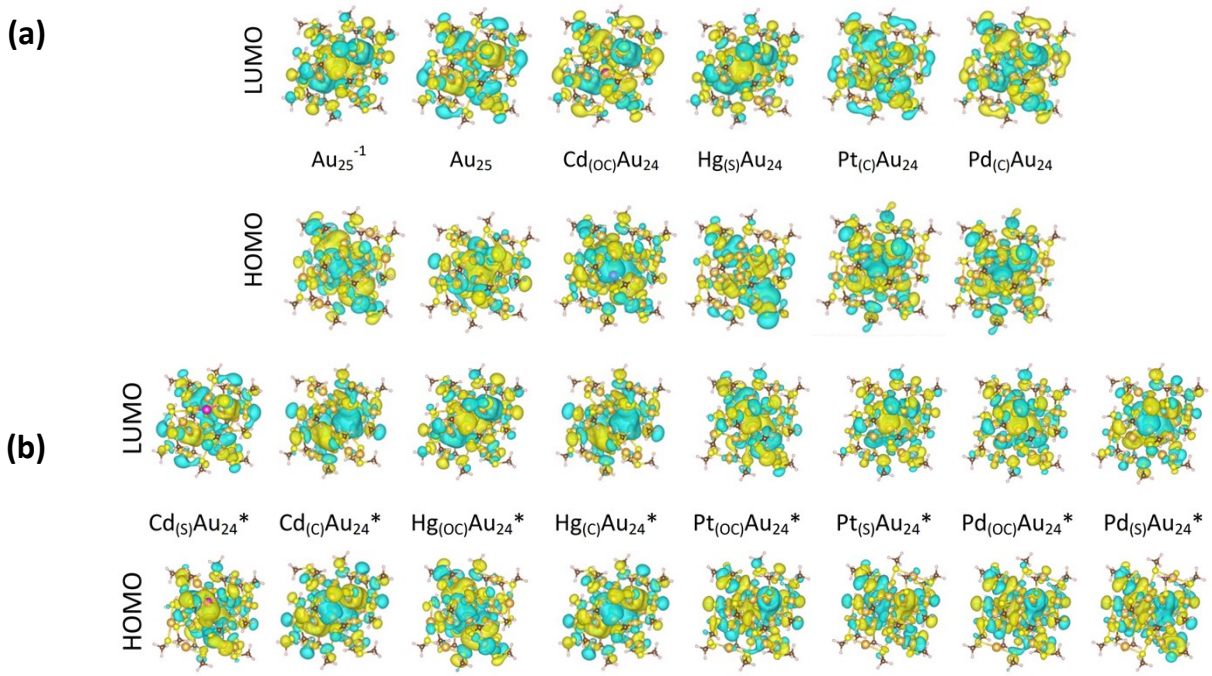

Figure S3. HOMO and LUMO of (a) experimentally determined TPNCs and (b) hypothetical TPNCs in their fully protected state. Hypothetical systems are labeled with *.

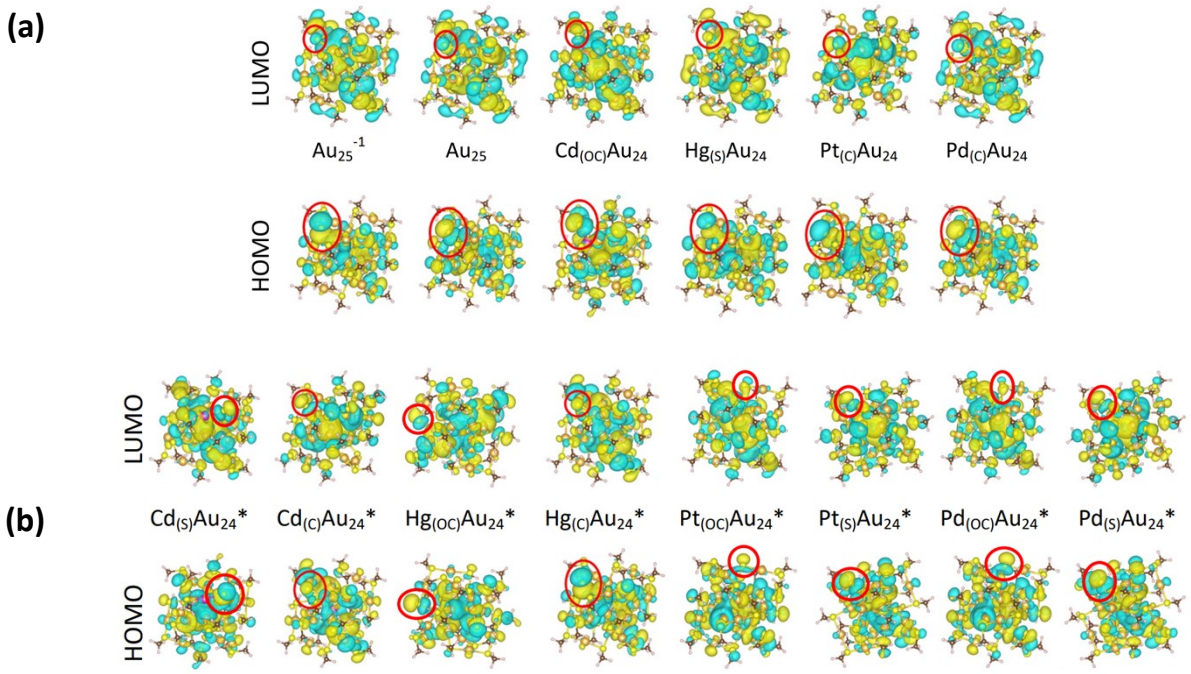

Figure S4. HOMO and LUMO of (a) experimentally determined TPNCs and (b) hypothetical TPNCs upon -R removal. Hypothetical systems are labeled with *.

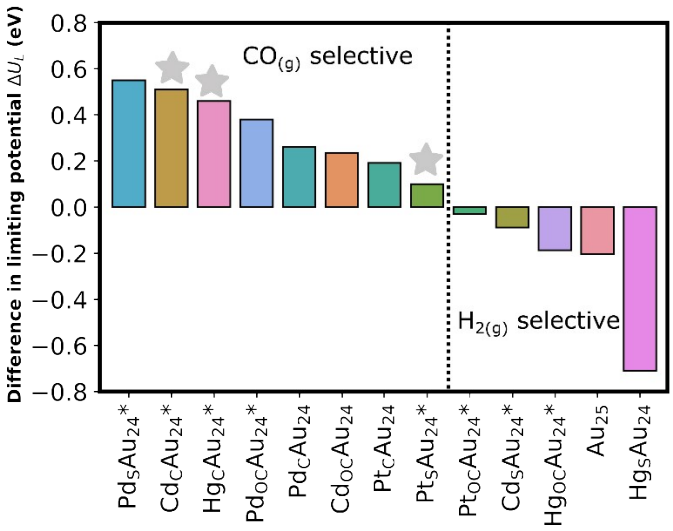

Figure S5. Difference in limiting potentials (ΔU_L) of CO_2R vs. HER on the S active sites of the different TPNCs. Positive values reflect selectivity towards $CO_{(g)}$ formation while negative values reflect selectivity towards $H_{2(g)}$ formation. Dashed line separates TPNCs selective towards $CO_{(g)}$ (left) or $H_{2(g)}$ formation (right). *CO formation is the limiting potential on TPNCs with a grey star.

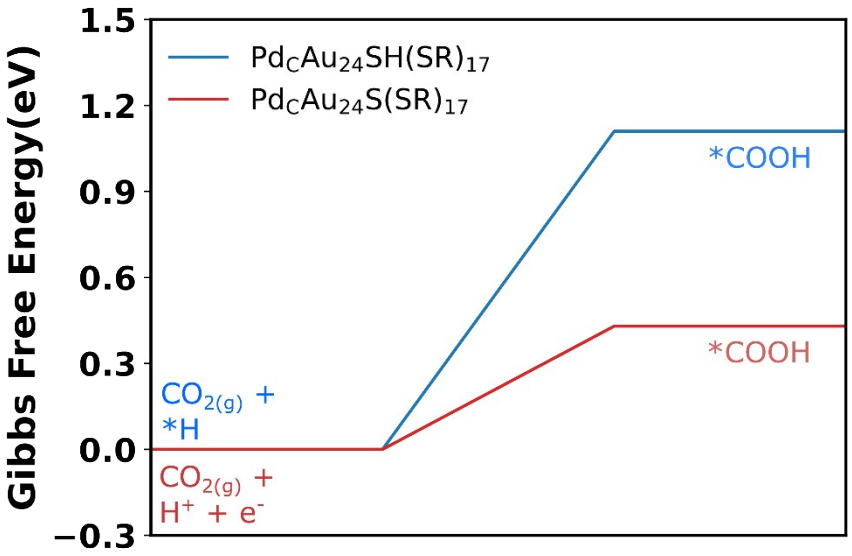

Figure S6. *COOH formation energy on S active sites of $Pd_{(C)}Au_{24}$ when it is formed via *H bound on the S site (blue line) or via proton coupled electron transfer ($H^+ + e^-$, red line)

TPNC	**Bader charge of S active site in fully protected TPNC**	**Bader charge of S active site in -R removed TPNC**
Au_{25}	-0.05	-0.30
$Cd_{(OC)}Au_{24}$	-0.07	-0.51
$Cd_{(S)}Au_{24}$*	-0.22	-0.53
$Cd_{(C)}Au_{24}$*	-0.07	-0.30
$Hg_{(OC)}Au_{24}$*	-0.09	-0.41
$Hg_{(S)}Au_{24}$	-0.07	-0.36
$Hg_{(C)}Au_{24}$*	-0.07	-0.30
$Pt_{(OC)}Au_{24}$*	-0.03	-0.25
$Pt_{(S)}Au_{24}$*	-0.05	-0.22
$Pt_{(C)}Au_{24}$	-0.04	-0.28
$Pd_{(Oc)}Au_{24}$*	-0.10	-0.30
$Pd_{(S)}Au_{24}$*	-0.08	-0.27
$Pd_{(C)}Au_{24}$	-0.03	-0.25

Table S1. Bader charge comparison of fractional charge on S active site on the fully protected TPNC vs -R removed TPNC. More negative number implies higher electron density on the S active site.

TPNC	***CO formation (eV)**	**Difference in limiting potentials (ΔU_L, ev)**
$Hg_{(C)}Au_{24}$*	0.36	0.46
$Cd_{(C)}Au_{24}$*	0.28	0.51
$Pt_{(S)}Au_{24}$*	0.19	0.10

Table S2. *CO formation energies along with difference in limiting potentials (ΔU_L) for TPNCs with *CO formation as the limiting potential. In the above three cases, ΔU_L = G (*CO formation) – G (*H formation). In all other cases, ΔU_L = G (*COOH formation) – G (*H formation)