

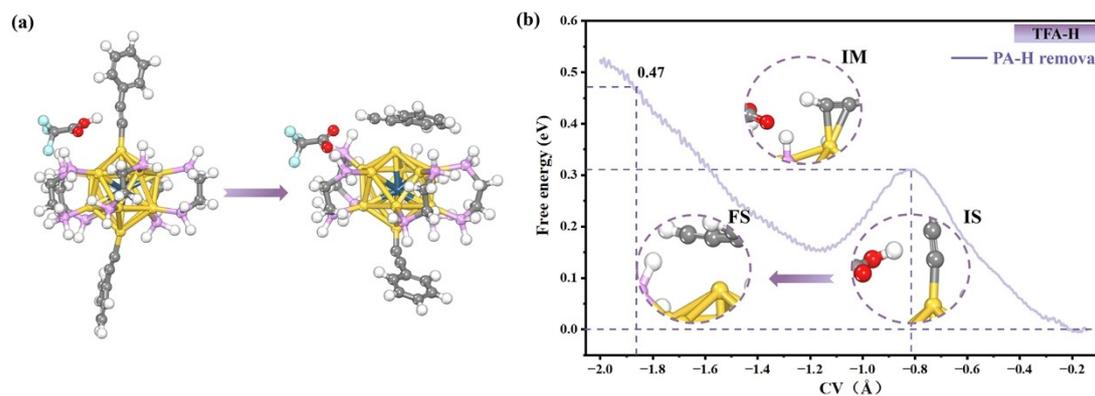
## **Supporting Information**

### **Computational Exploration on the N-heterocyclic Carbene (NHC)- for-Phenylacetylene Ligand Exchange in IrAu<sub>12</sub> Alloy Clusters**

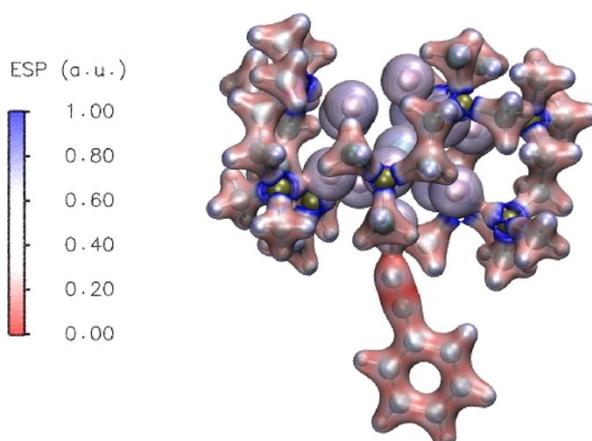
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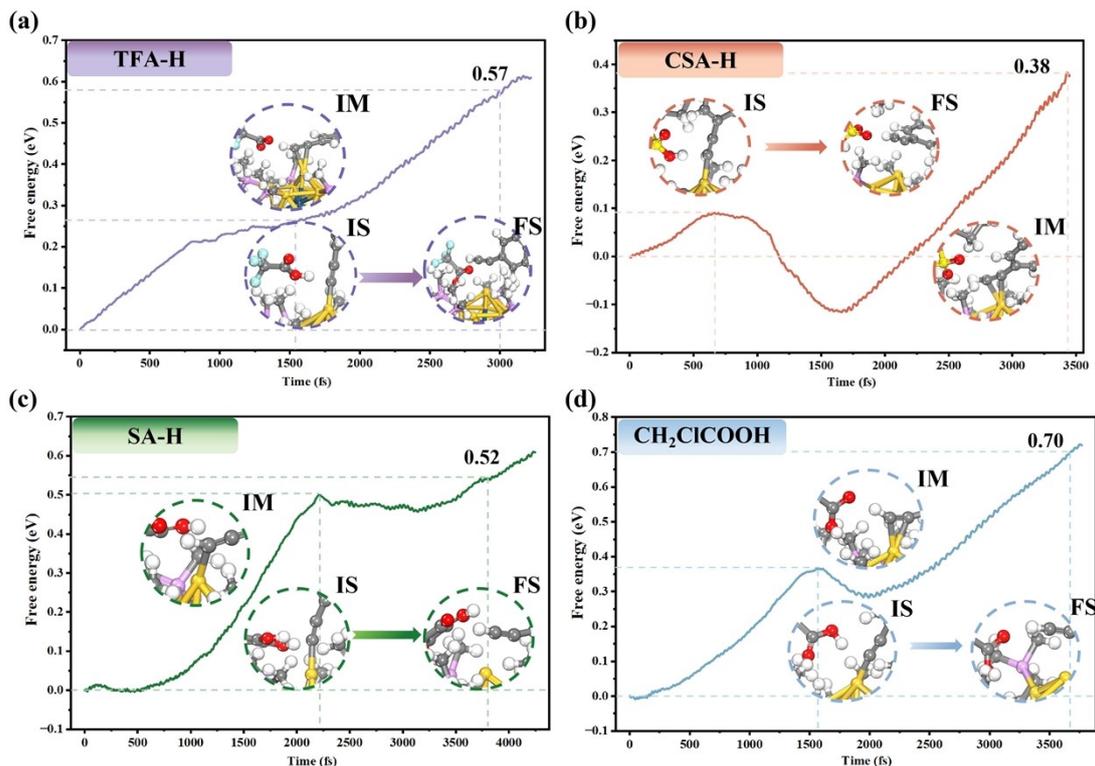
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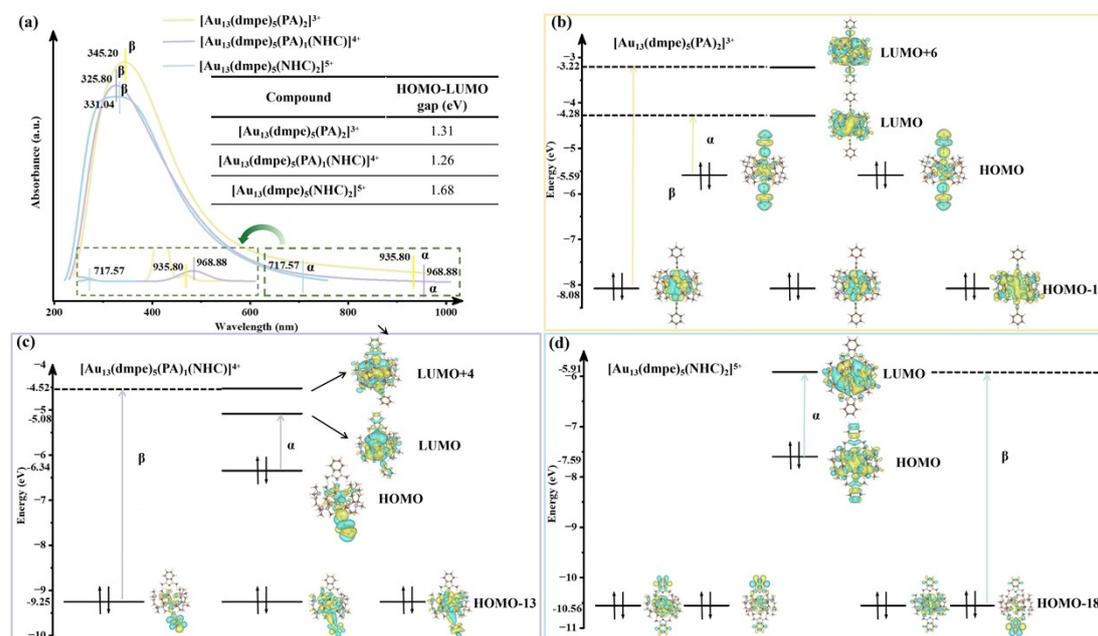
**Figure S1.** (a) Schematic of PA removal from  $[\text{IrAu}_{12}(\text{ppe})_5(\text{PA})_2]^+$  under TFA-H attack. (b) Free energy change curve for the removal of the first PA ligand in the  $[\text{IrAu}_{12}(\text{ppe})_5(\text{PA})_2]^+$  cluster under TFA-H acid attack.



**Figure S2.** The electrostatic potential over the van der Waals surface (density=0.001 a.u.) of  $[\text{IrAu}_{12}(\text{dmpe})_5(\text{PA})_1]^{2+}$  intermediate.



**Figure S3.** Time-dependent free energy profiles from AIMD simulations of the PA removal process under different acidic conditions.



**Figure S4.** Optical and electronic properties of  $\text{Au}_{13}$  clusters. (a) Simulated UV-vis absorption spectra for  $[\text{Au}_{13}(\text{dmpc})_5(\text{PA})_2]^{3+}$  (yellow line),  $[\text{Au}_{13}(\text{dmpc})_5(\text{PA})_1(\text{NHC})]^{4+}$  (purple line) and  $[\text{Au}_{13}(\text{dmpc})_5(\text{NHC})_2]^{5+}$  (blue line). The inset shows the HOMO-LUMO gap of the three clusters. Frontier orbitals involved in the  $\alpha$  and  $\beta$  transitions of  $[\text{Au}_{13}(\text{dmpc})_5(\text{PA})_2]^{3+}$  (b),

$[\text{Au}_{13}(\text{dmpe})_5(\text{PA})_1(\text{NHC})]^{4+}$  (c) and  $[\text{Au}_{13}(\text{dmpe})_5(\text{NHC})_2]^{5+}$  (d).