Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Supplementary Information

# 18-electron rule inspired Zintl-like ions composed of all transition metals

## 1. Band structure of $Mg_2(FeH_6)$ crystal.

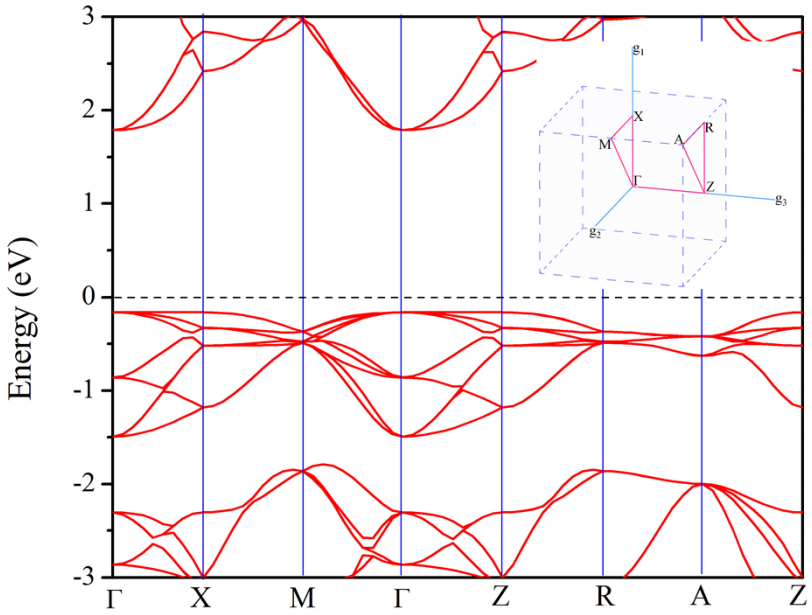



**Figure S1.** Band structure of $Mg_2(FeH_6)$ crystal. Corresponding first Brillouin zone and the high symmetry K point paths are shown in the inset: Γ (0, 0, 0) → X (1/2, 0, 0) → M (1/2, 1/2, 0)→ Γ (0, 0, 0) → Z (0, 0, 1/2) → R (1/2, 0, 1/2) → A (1/2, 1/2, 1/2) → Z (0, 0, 1/2).

**2. Geometric structure of $Mg_2(FeAu_6)$ crystal.**

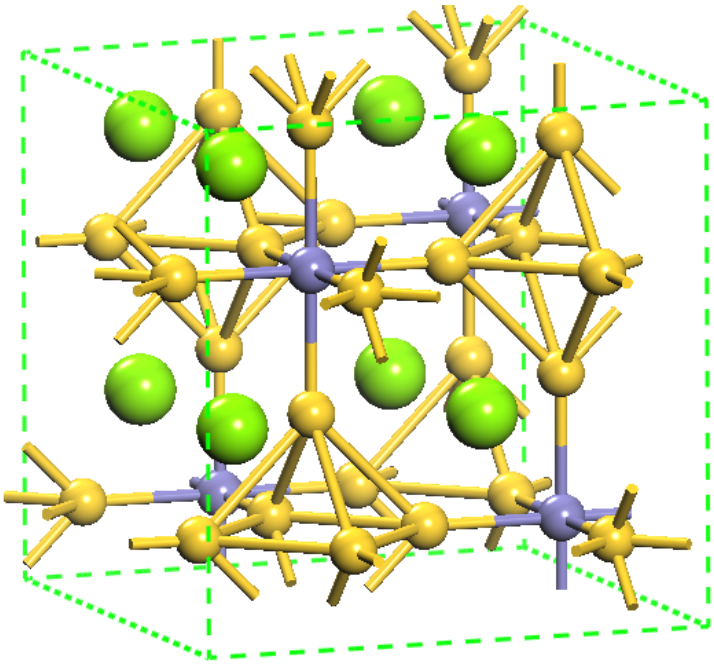


**Figure S2.** Structure of $Mg_2(FeAu_6)$ crystal. Cyan, green, and yellow atoms are Mg, Fe, and Au, respectively.

### 3. IR and Raman Spectra of $I_h$ and $O_h$ Isomers of $[Ti@Au_{12}]^{2-}$.

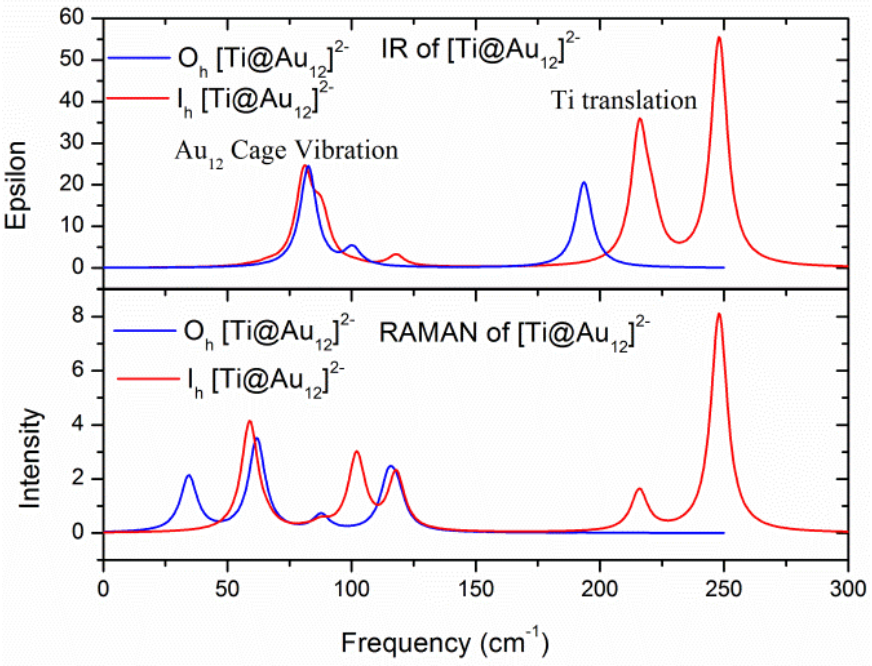



**Figure S3.** Comparison of IR and Raman spectra between $I_h$ and $O_h$ isomers of $[Ti@Au_{12}]^{2-}$.

## 4. Molecular dynamic simulations of $Ti@Au_{12}$ and $Na_2[Ti@Au_{12}]$.

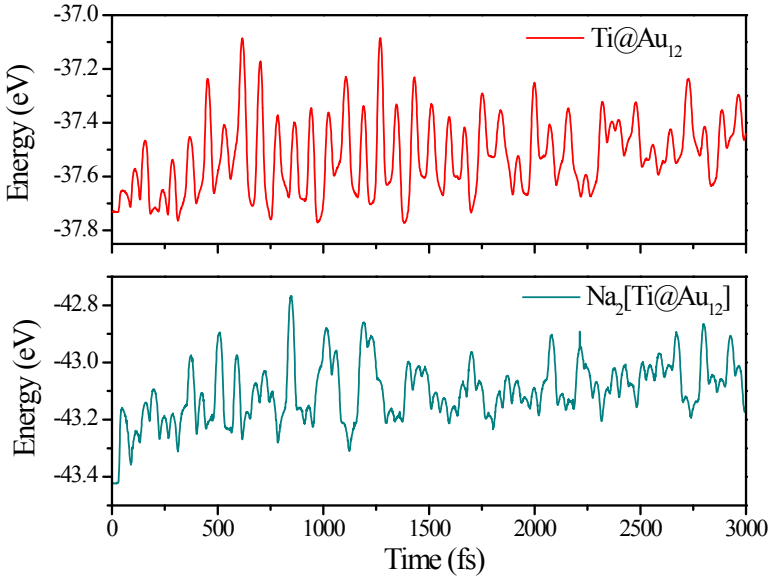



**Figure S4.** *Ab initio* molecular dynamic simulation showing total energy fluctuations of $Ti@Au_{12}$ and $Na_2[Ti@Au_{12}]$ with respect to time at 300 K.

## 5. Partial density of states of $Na_2[Ti@Au_{12}]$.

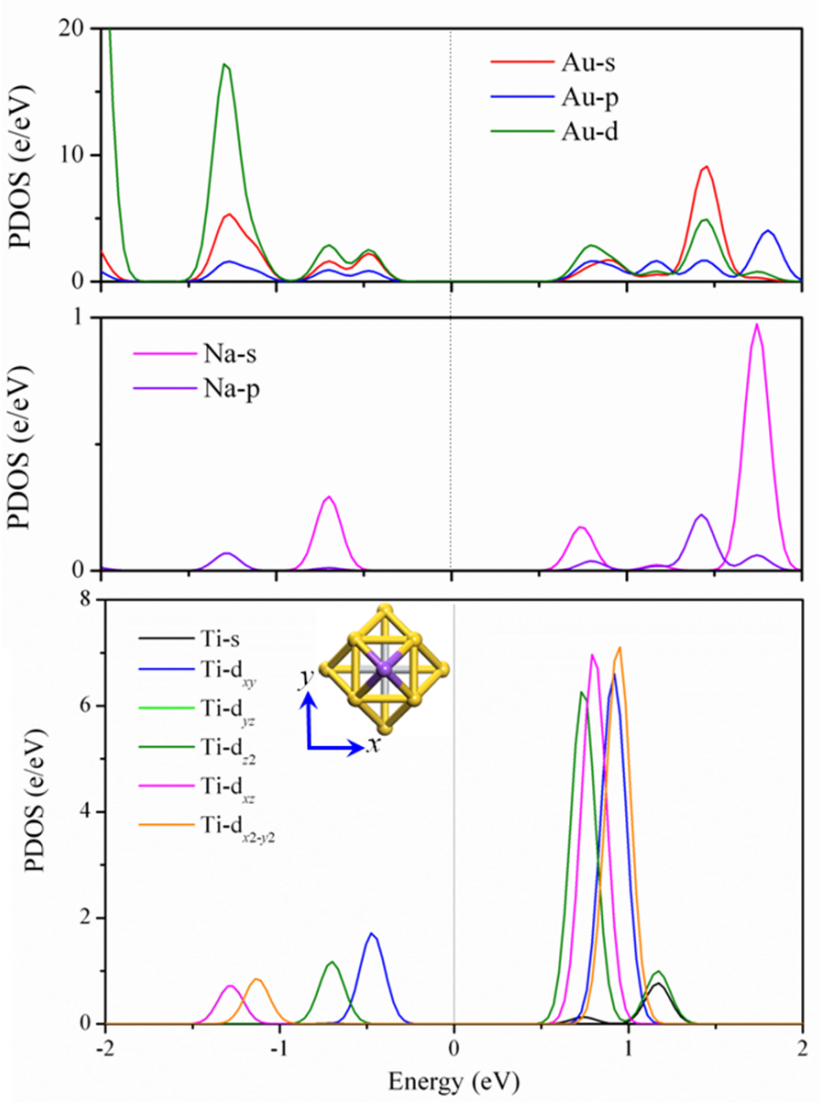



**Figure S5.** PDOS plot of $Na_2[Ti@Au_{12}]$-$D_{4h}$. The directions are defined as shown in the inset.

## 6. Selected isomers of $Cs_2[Ti@Au_{12}]$ and $Mg[Ti@Au_{12}]$.

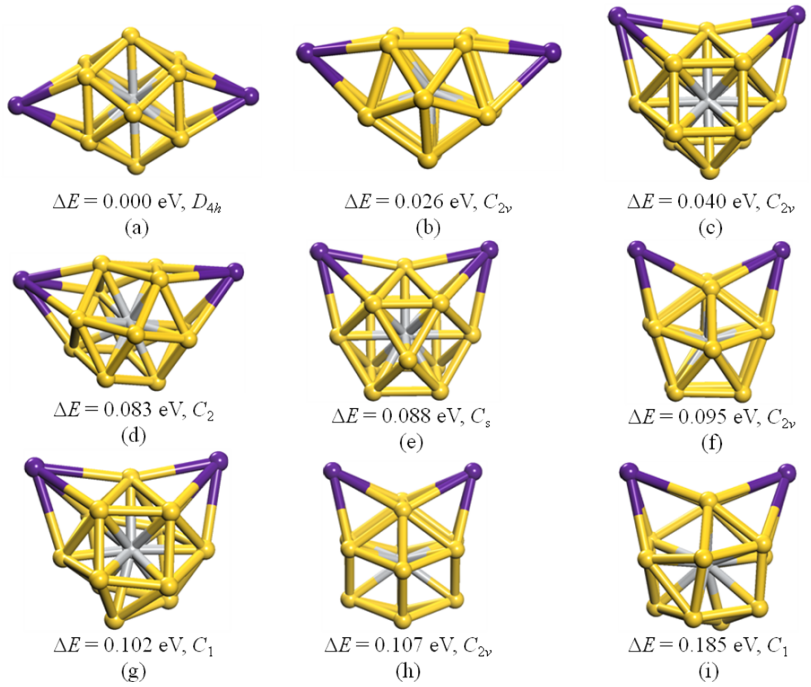



**Figure S6.** Several low energy isomers of $Cs_2[Ti@Au_{12}]$ along with their relative energies $\Delta E$ and symmetry point group. The yellow, purple, and light grey spheres represent Au, Cs, and Ti, respectively.

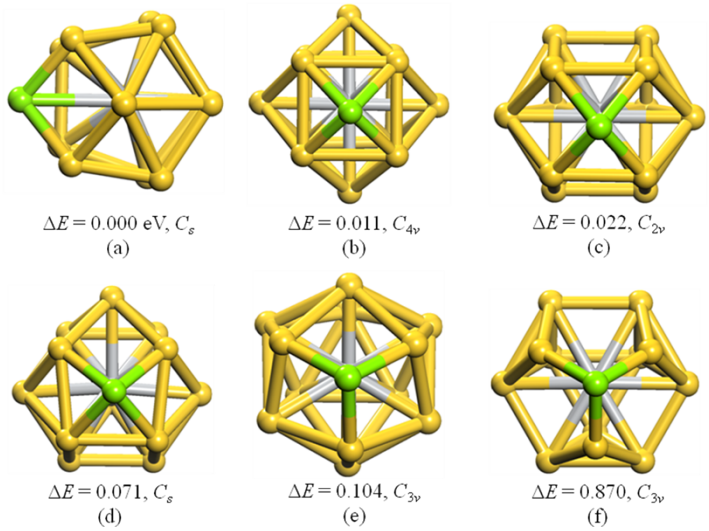
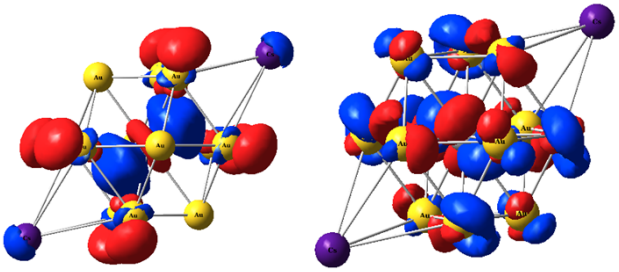



**Figure S7.** Several low energy isomers of $Mg[Ti@Au_{12}]$. The yellow, green, and light grey spheres represent Au, Mg, and Ti, respectively.

## 7. Molecular Orbitals (HOMO/LUMO) of $Cs_2[TiAu_{12}]$.



LUMO HOMO

$Cs_2Ti@Au_{12}$

**Figure S8.** HOMO and LUMO molecular orbitals of $Cs_2[Ti@Au_{12}]$.