Supplementary Information for:

Structure, optical properties, and catalytic applications of alkynyl-protected M_4Rh_2 (M = Ag/Au) nanoclusters with atomic precision: A comparative study

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‡ L. Chen and F. Sun contributed equally to this work.

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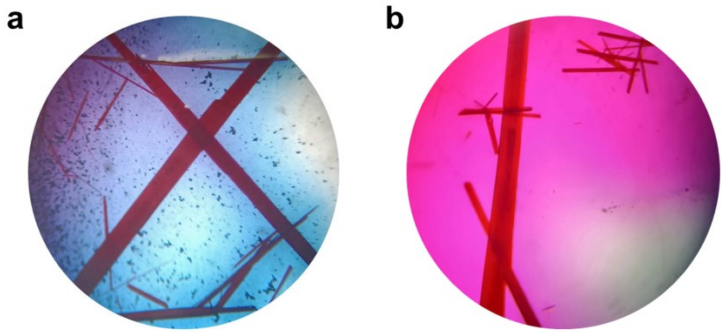

Figure S1. The images of (a) Ag_4Rh_2 and (b) Au_4Rh_2 crystals under an optical microscope.

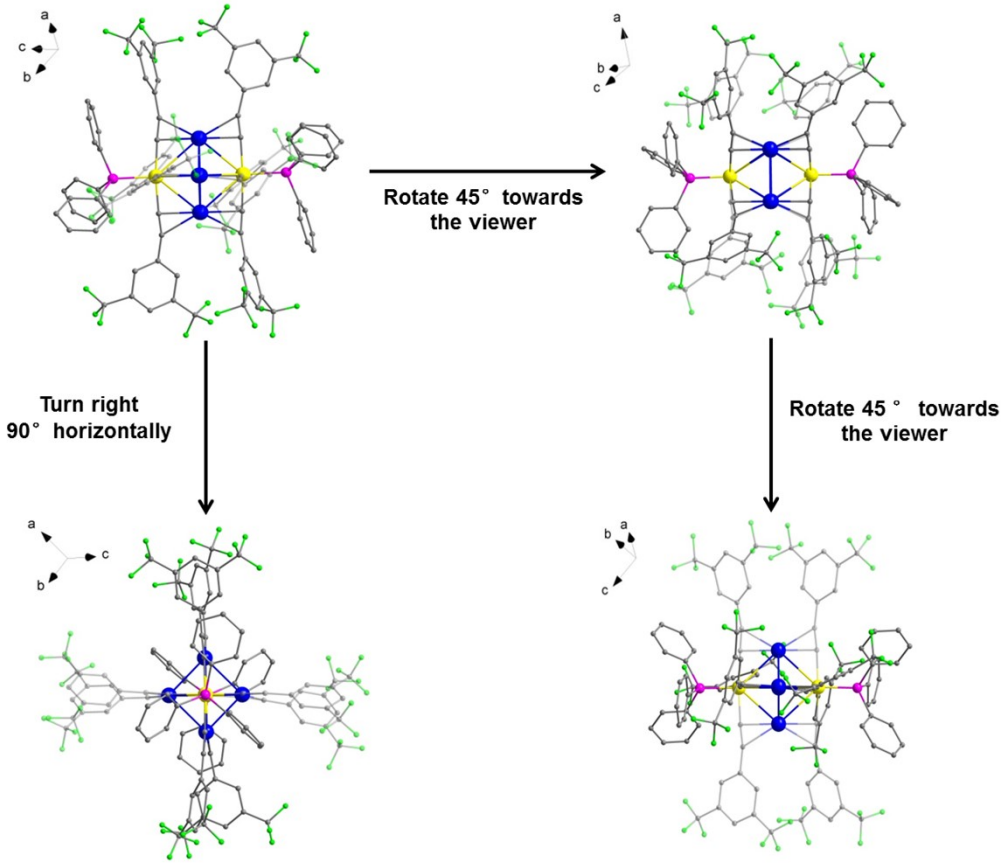

Figure S2. Spatial arrangement of Ag_4Rh_2 in different spatial orientations. Color code: Ag, bule; Rh, yellow; C, gray; F, green; P, pink. All hydrogen atoms are omitted for clarity.

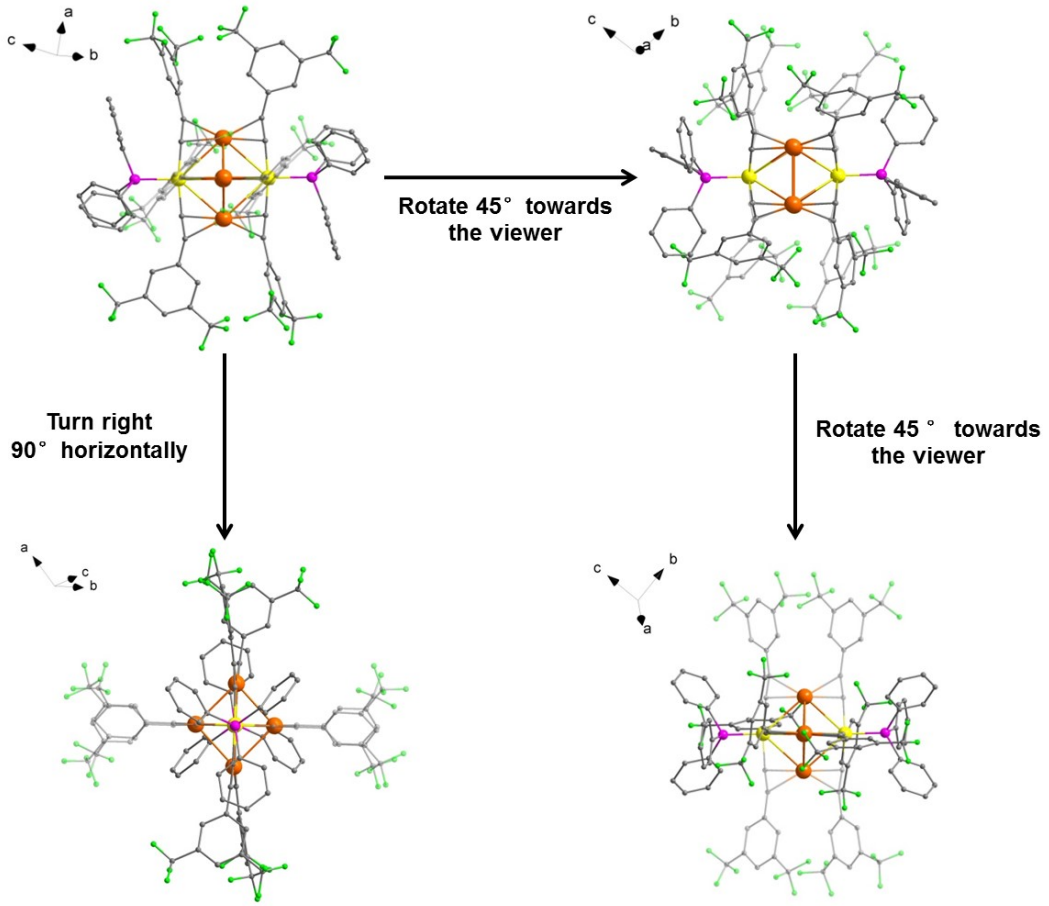

Figure S3. Spatial arrangement of Au_4Rh_2 in different spatial orientations. Color code: Au, orange; Rh, yellow; C, gray; F, green; P, pink. All hydrogen atoms are omitted for clarity.

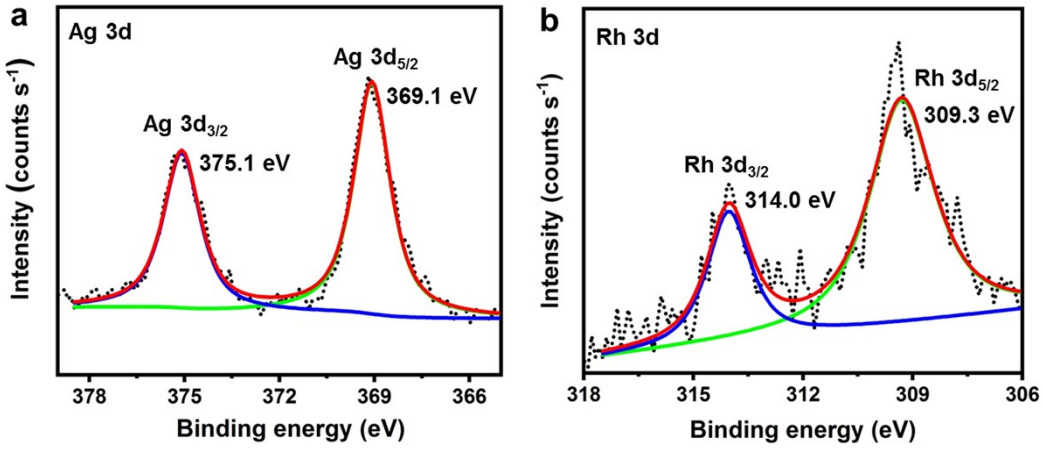

Figure S4. The core-level (a) Ag 3d and (b) Rh 3d XPS spectra of Ag_4Rh_2.

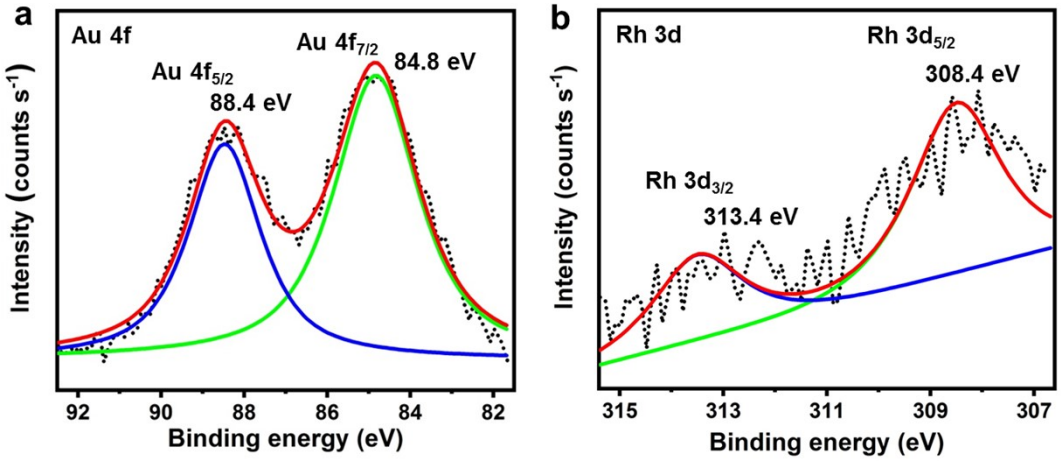

Figure S5. The core-level (a) Au 4f and (b) Rh 3d XPS spectra of Au_4Rh_2.

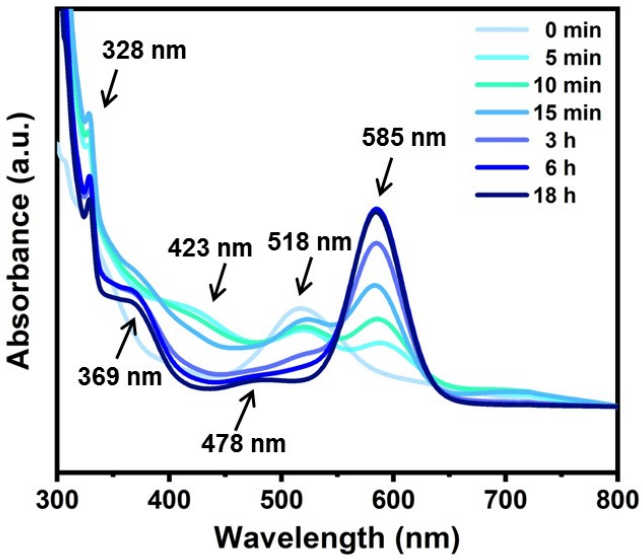

Figure S6. Time-dependent UV-vis absorption spectra of the conversion of Ag_{32} to Ag_4Rh_2.

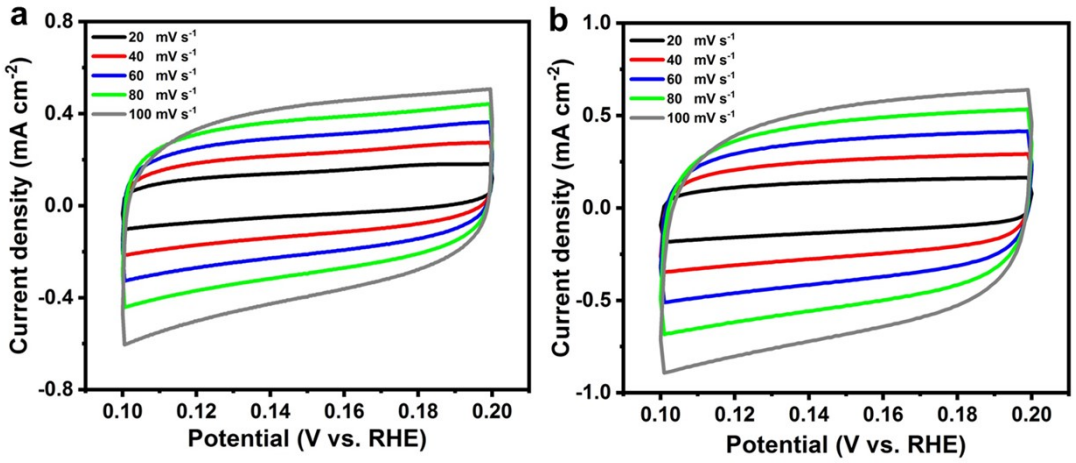

Figure S7. CV curves at different scan rates (20 to 100 mV s^{-1}) for (a) Ag_4Rh_2 and (b) Au_4Rh_2.

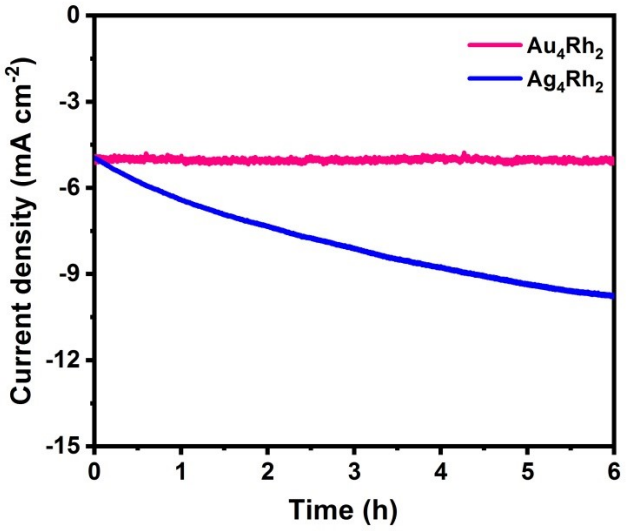

Figure S8. Stability test of Ag_4Rh_2 (blue) and Au_4Rh_2 (pink) in HER.

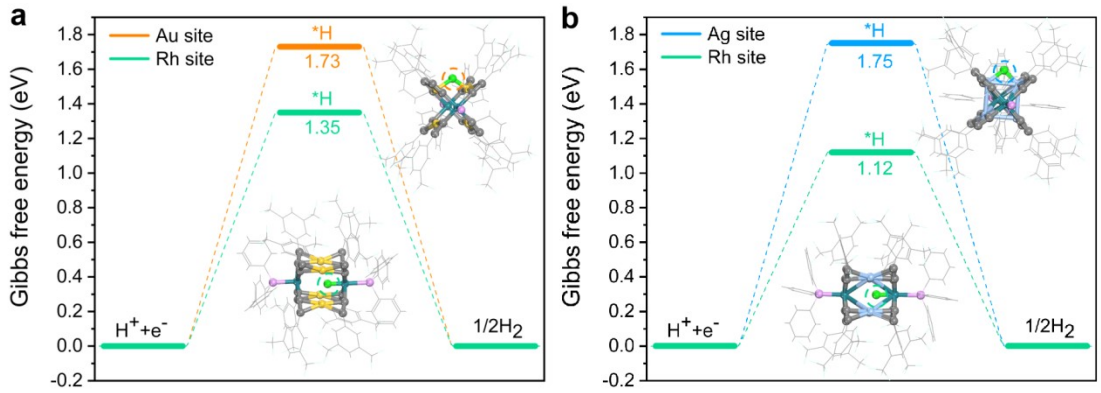

Figure S9. Calculated free-energy diagrams for the HER on intact (a) Au_4Rh_2 and (b) Ag_4Rh_2 at zero applied potential. The inset shows the corresponding optimized structure of a *H-adsorbed. Color code: Au, yellow; Ag, sky blue; Rh, navy blue; P, pink; C, gray; F, cyan; H, white; H*, green. Ligand chains are shown in a linear pattern for clarity.

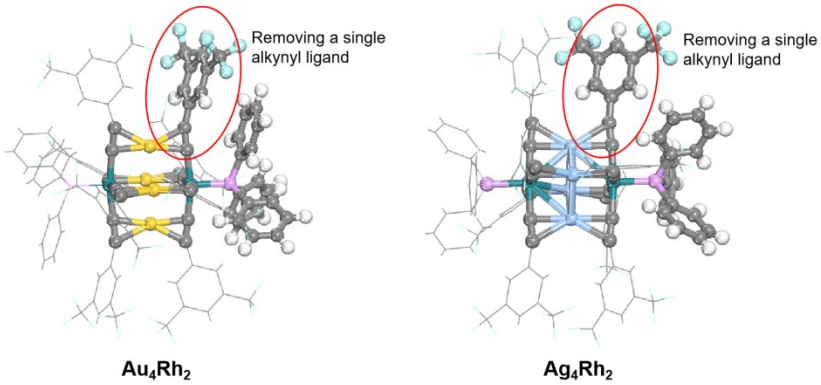

Figure S10. The single alkynyl ligand for removal on Au_4Rh_2 and Ag_4Rh_2 is circled in red. Color code: Au, yellow; Ag, sky blue; Rh, navy blue; P, pink; C, gray; F, cyan; H, white.

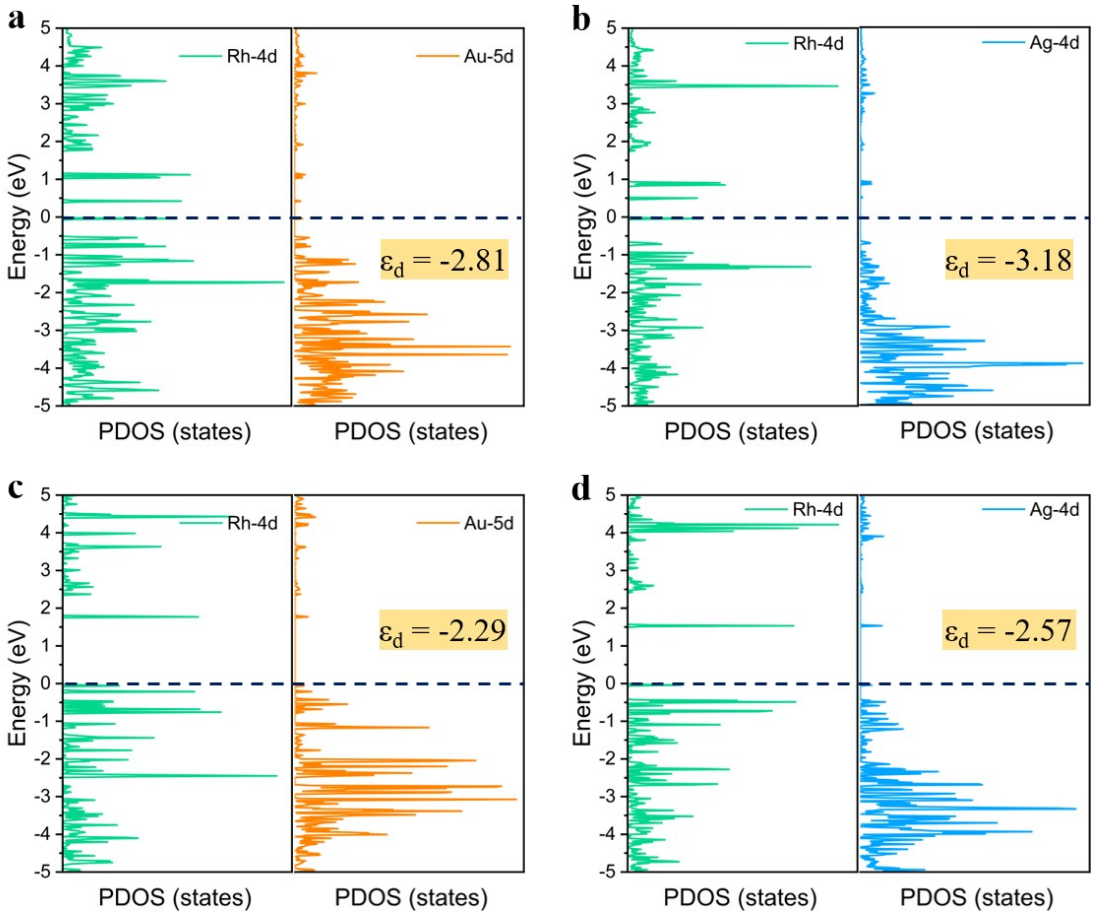

Figure S11. PDOS of the metal d-states in (a) Au_4Rh_2, (b) Ag_4Rh_2, (c) deligated-Au_4Rh_2, and (d) deligated-Ag_4Rh_2 clusters. Of note, the Fermi energy levels have been normalized to zero (black dotted line).

Table S1. Crystal data and structure refinement for Ag_4Rh_2.

Chemical formula	$C_{116}H_{54}Ag_4F_{48}P_2Rh_2$
Formula weight	6585.32
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	27.0491(3)
b/Å	29.5409(3)
c/Å	34.5184(4)
α/°	90.0
β/°	111.6840(10)
γ/°	90.0
V/Å^3	25630.3(5)
Z	4
ρ_{calc}g/cm^3	1.707
μ/mm^{-1}	8.157
F(000)	12932
Crystal size/mm^3	0.70 × 0.10 × 0.08
Radiation	Cu K_α (λ = 1.54178)
2Θ range for data collection/°	6.006 to 148.604
Index ranges	-33 ≤ h ≤ 23, -36 ≤ k ≤ 36, -42 ≤ l ≤ 42
Reflections collected	108374
Independent reflections	50559 [R_{int} = 0.0455, R_{sigma} = 0.0625]
Data/restraints/parameters	50559/8282/3624
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0730, wR_2 = 0.1707
Final R indexes [all data]	R_1 = 0.1053, wR_2 = 0.1984
Largest diff. peak/hole/e Å^{-3}	2.070/ -1.573

Table S2. Crystal data and structure refinement for Au_4Rh_2.

Chemical formula	$C_{116}H_{54}Au_4F_{48}P_2Rh_2$
Formula weight	3691.62
Temperature/K	120(2)
Crystal system	triclinic
Space group	*P*1
a/Å	17.16177(18)
b/Å	17.24053(19)
c/Å	24.4066(2)
α/°	90.3557(8)
β/°	103.8441(8)
γ/°	115.4022(10)
V/Å^3	6284.73(12)
Z	2
ρ_{calc}g/cm^3	1.951
μ/mm^{-1}	5.057
F(000)	3536
Crystal size/mm^3	0.10 × 0.03 × 0.03
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.482 to 62.050
Index ranges	-24 ≤ h ≤ 24, -24 ≤ k ≤ 23, -33 ≤ l ≤ 34
Reflections collected	183311
Independent reflections	33635 [R_{int} = 0.0541, R_{sigma} = 0.0469]
Data/restraints/parameters	33635/2284/2053
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0378, wR_2 = 0.0868
Final R indexes [all data]	R_1 = 0.0604, wR_2 = 0.0951
Largest diff. peak/hole/e Å^{-3}	1.872/-2.887