Supplementary Information for

The Smallest Superatom $Au_4(PPh_3)_4I_2$ with Two Free Electrons: Synthesis, Structure Analysis, and Electrocatalytic Conversion of CO_2 to CO

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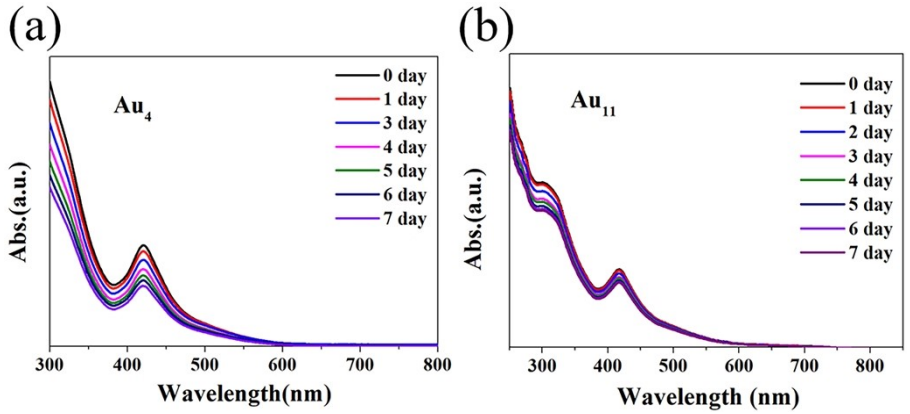

Fig S1. UV-vis absorbance spectra of (a) **Au_4** and (b) **Au_{11}** in CH_2Cl_2 for one week at room temperature

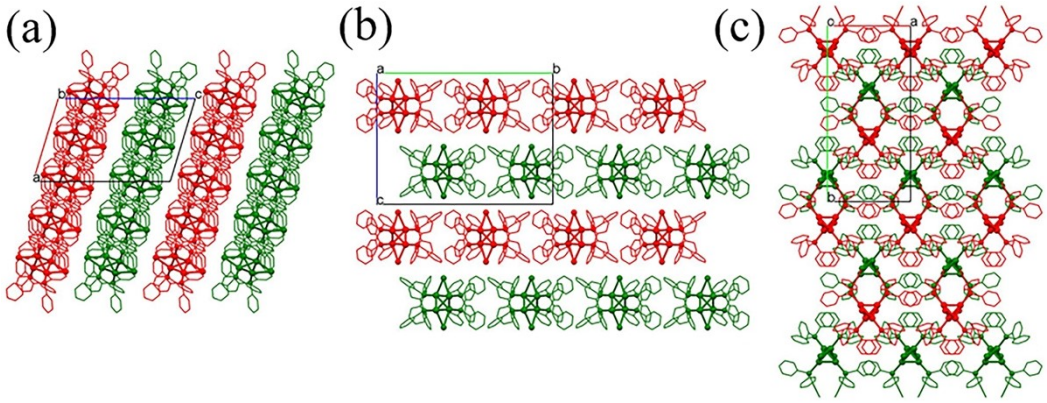

Fig S2. Packing mode of Au_4 in the crystal shown along an axis (a), b axis (b) and c axis (c). The two enantiomers are shown in different colors.

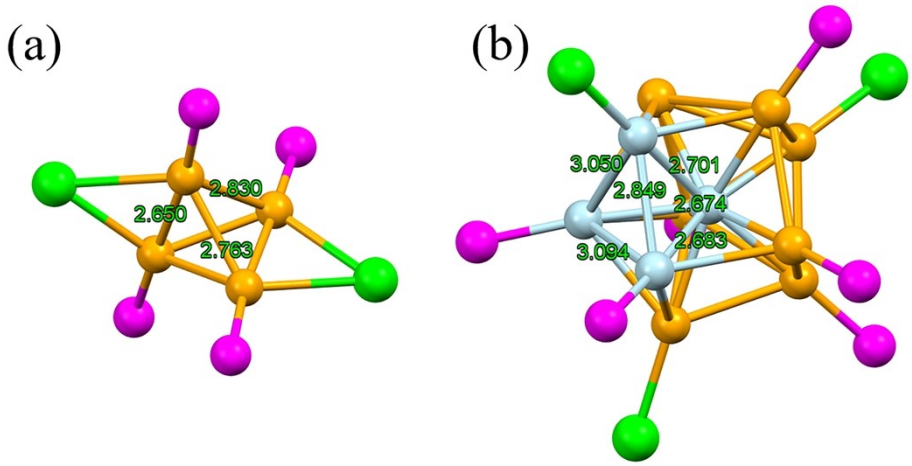

Fig S3. The Au-Au bond lengths in the (a) **Au_4** and (b) **Au_{11}**. (Color labels: yellow and light blue = Au, pink = P, green = I, for charity all C and H atoms are not shown.)

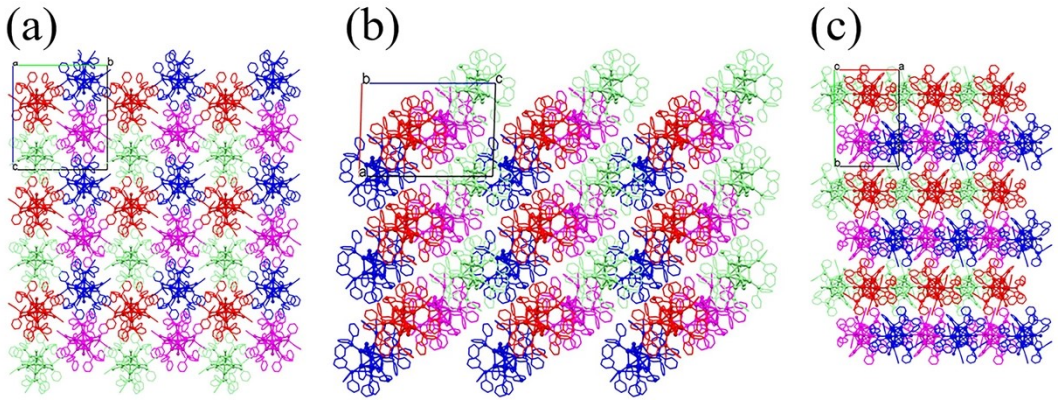

Fig S4. Packing mode of Au_{11} in the crystal shown along an axis (a), b axis (b) and c axis (c). The three enantiomers are shown in different colors.

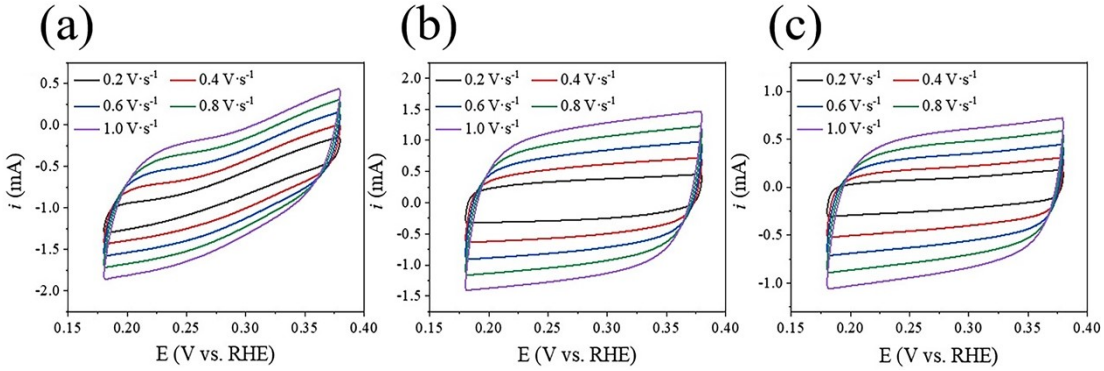

Fig S5. Cyclic voltammetry of (a) **Au(I)P**, (b) **Au_4** and (c) **Au_{11}** in 0.5 M $KHCO_3$ electrolyte at a scan rate from 0.02 (black), 0.04 (red), 0.06 (blue), 0.08 (green), 0.1 (purple) $V \cdot s^{-1}$.

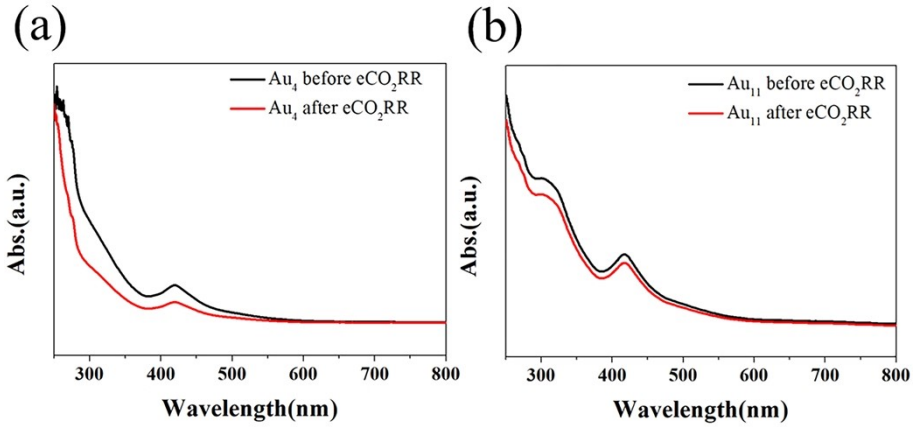

Fig S6. UV-vis absorbance spectra of **Au_4** and **Au_{11}** before and after eCO_2RR.

Table S1. The crystal structure parameters for $Au_4(PPh_3)_4I_2$.

Identification code	$Au_4(PPh_3)_4I_2$
Empirical formula	$C_{72}H_{60}Au_4I_2P_4$
Formula weight	2090.74
Temperature/K	149.99(10)
Crystal system	Monoclinic
Space group	C2/c
a/Å	12.8328(6)
b/Å	25.9977(10)
c/Å	20.2930(9)
α/°	90
β/°	106.861(4)
γ/°	90
Volume/Å^3	6479.1(5)
Z	4
ρ_{calc}g/cm^3	2.143
μ/mm^{-1}	10.123
F(000)	3896.0
Crystal size/mm^3	0.06 × 0.05 × 0.05
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.194 to 62.482
Index ranges	-15 ≤ h ≤ 17, -37 ≤ k ≤ 28, -25 ≤ l ≤ 22
Reflections collected	18072
Independent reflections	7931 [R_{int} = 0.0456, R_{sigma} = 0.0630]
Data/restraints/parameters	7931/0/298
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0364, wR_2 = 0.0733
Final R indexes [all data]	R_1 = 0.0539, wR_2 = 0.0781
Largest diff. peak/hole / e Å^{-3}	2.27/-1.25

Table S2. Average bond length of **Au_4** and **Au_{11}**.

Clusters	Au-Au (Å)	Au-P (Å)	Au-I (Å)
Au_4	2.740	2.287	2.935
Au_{11}	2.875	2.282	2.600