Supporting Information for:

$Au_{22}(L^8)_6$ Nanocluster with *in situ* Uncoordinated Au as Highly Active Catalyst for O_2 Activation and CO Oxidation

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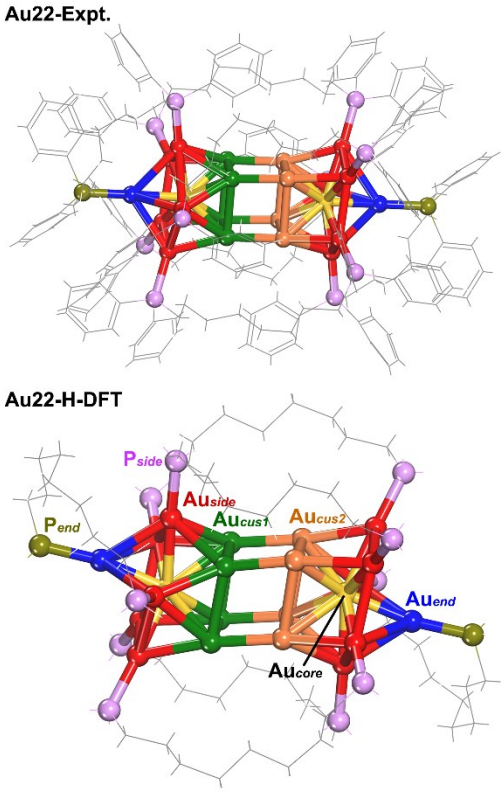

Length (Å)	Au22-Expt.	Au22-DFT	Au22-H-DFT
$Au_{cus1(2)}$-$Au_{cus1(2)}$	2.850	2.935	2.991
Au_{cus1}-Au_{cus2}	2.647	2.646	2.623
Au_{side}-Au_{side}	3.043	3.141	3.091
Au_{core}-$Au_{cus1(2)}$	2.728	2.922	2.877
Au_{core}-Au_{side}	2.654	2.715	2.685
Au_{core}-Au_{end}	2.631	2.635	2.637
Au_{side}-P_{side}	2.496	2.321	2.281
Au_{end}-P_{end}	2.296	2.291	2.270

Fig. S1. The geometric structures and bond parameters of $Au_{22}(L^8)_6$ nanocluster, where Au_{22}-Expt. and Au_{22}-DFT denotes the experimental and DFT-optimized structure based

on the experimental L^8 ligands, $Au_{22}(L^8)_6$, where L^8 = 1,8-bis(diphenylphosphino) octane, while Au_{22}-H-DFT represents the simplified model by replacing the bulky phenyl groups of the L^8 ligands with H atoms.

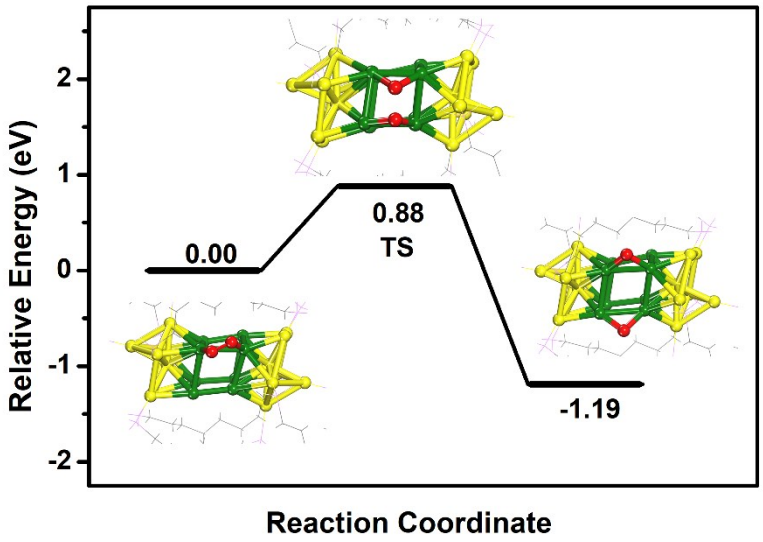

Fig. S2. The reaction pathway for dissociation of the chemisorbed O_2 on $Au_{22}(L^8)_6$ calculated at the GGA+U level (U_{eff} = 5.0 eV).

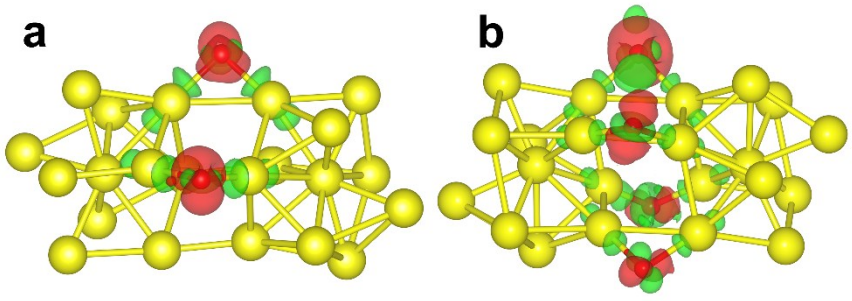

Fig. S3. The charge density difference of $Au_{22}(L^8)_6$ with two and four adsorbed O atoms, $Au_{22}(L^8)_6O_2$ for (a) and $Au_{22}(L^8)_6O_4$ for (b). The red and green region represents the electron accumulation and depletion, respectively.