Supplementary information for

Relativistic DFT Investigation of Electronic Structure Effects Arising from Doping the Au_{25} Nanocluster with Transition Metals

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Population analysis of low-lying molecular orbitals in different isomers of MAu_{24}^{-3}

For a better understanding of the nature of molecular orbitals (MOs), the doped species and the resulting contributions to MOs are divided into the following fragments; a) the dopant atom (M) b) Au_{12} or Au_{13} core and c) the ligands. These fragments are illustrated in Figure S1 for the case of isomer II. In this interaction picture, low-lying energy levels are originated from the mixing of; atomic d orbitals of dopant, P and D super-atomic orbitals of Au_{12} (or Au_{13}) core, and the orbitals that are localized on the ligand shell. Table S1 shows the contribution of each fragment orbitals to the MOs for different isomers and for different dopants. The contributions from dopant s or p orbitals are quite small, (less than 1% in most cases) and are not tabulated in Table S1.

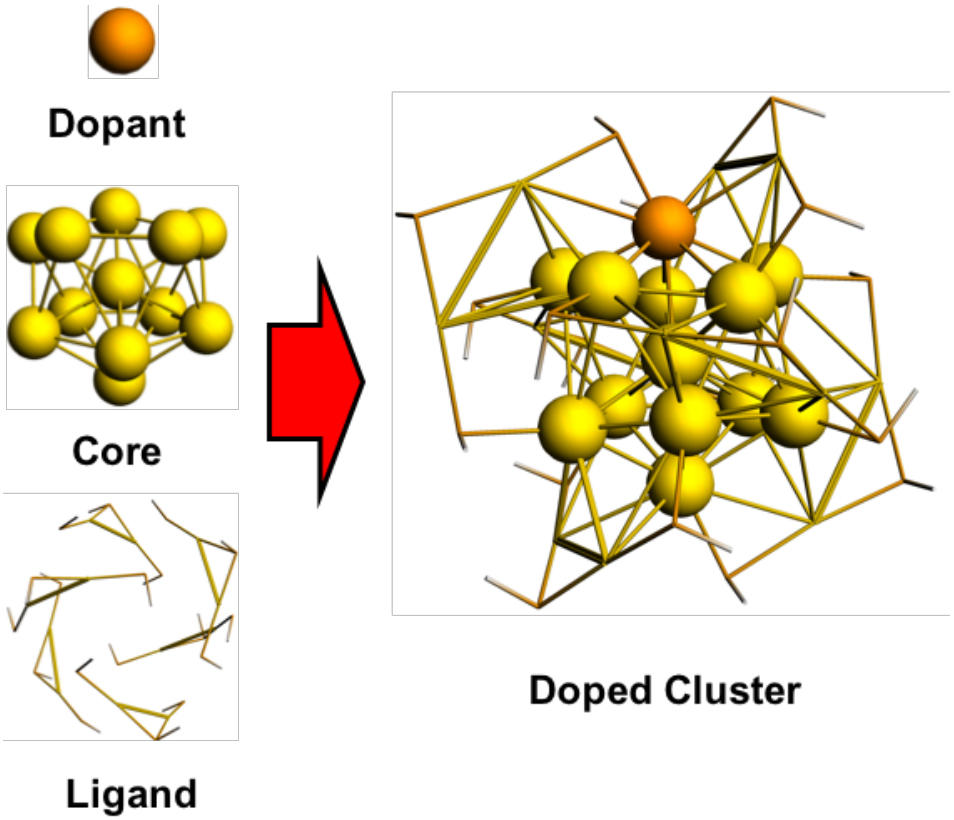

Figure S1. An example of the fragments employed in the population analysis of doped clusters for the isomer II structure. Fragments in this case consist of the dopant atom, Au_{12}^{+4} core and $Au_{12}(SH)_{18}^{-6}$ ligand shell. Note that in the case of isomer III, the core fragment becomes Au_{13}^{+5} while the ligand fragment is $Au_{11}(SH)_{18}^{-7}$.

Table S1. Coefficients of Fragment Orbitals for the Low-Lying MOs of Doped Systems

MO	Dopant d	Au_{12} core 1P	Au_{12} core 1D	Au d + thiolate	Label
Isomer I					
$CoAu_{24}^{-3}$					
HOMO-7	0%	55%	0%	28%	$1P^6$
HOMO-6	0%	54%	0%	30%	$1P^6$
HOMO-5	0%	54%	0%	27%	$1P^6$
HOMO-4	57%	0%	20%	5%	nd^{10}
HOMO-3	58%	0%	19%	5%	nd^{10}
HOMO-2	68%	0%	13%	3%	nd^{10}
HOMO-1	60%	0%	17%	5%	nd^{10}
HOMO	61%	0%	16%	0%	nd^{10}
LUMO	23%	0%	41%	22%	$1D^{10}$
LUMO-1	23%	0%	40%	20%	$1D^{10}$
$RhAu_{24}^{-3}$					
HOMO-7	48%	0%	14%	5%	nd^{10}
HOMO-6	47%	0%	14%	6%	nd^{10}
HOMO-5	47%	0%	14%	6%	nd^{10}
HOMO-4	32%	0%	21%	16%	nd^{10}
HOMO-3	32%	0%	21%	16%	nd^{10}
HOMO-2	0%	58%	0%	32%	$1P^6$
HOMO-1	0%	58%	0%	32%	$1P^6$
HOMO	0%	55%	0%	30%	$1P^6$
LUMO	16%	0%	41%	24%	$1D^{10}$
LUMO-1	14%	0%	41%	24%	$1D^{10}$
$IrAu_{24}^{-3}$					
HOMO-7	42%	0%	18%	7%	nd^{10}
HOMO-6	42%	0%	17%	9%	nd^{10}
HOMO-5	41%	0%	16%	7%	nd^{10}
HOMO-4	29%	0%	23%	17%	nd^{10}
HOMO-3	29%	0%	24%	15%	nd^{10}
HOMO-2	0%	53%	0%	29%	$1P^6$
HOMO-1	0%	53%	0%	30%	$1P^6$
HOMO	0%	52%	0%	29%	$1P^6$
LUMO	17%	0%	36%	19%	$1D^{10}$
LUMO-1	16%	0%	35%	27%	$1D^{10}$
Isomer II					
$CoAu_{24}^{-3}$					
HOMO-7	17%	38%	2%	19%	$1P^6$
HOMO-6	7%	46%	1%	24%	$1P^6$
HOMO-5	5%	45%	0%	21%	$1P^6$
HOMO-4	43%	7%	12%	7%	nd^{10}

HOMO-3	73%	0%	4%	0%	nd^{10}
HOMO-2	37%	12%	18%	6%	nd^{10}
HOMO-1	73%	3%	3%	0%	nd^{10}
HOMO	75%	0%	1%	0%	nd^{10}
LUMO	20%	1%	36%	16%	$1D^{10}$
LUMO-1	14%	0%	42%	18%	$1D^{10}$
$RhAu_{24}^{-3}$					
HOMO-7	14%	31%	5%	18%	$1P^{6}$
HOMO-6	22%	40%	1%	15%	$1P^{6}$
HOMO-5	5%	44%	0%	28%	$1P^{6}$
HOMO-4	67%	1%	2%	1%	nd^{10}
HOMO-3	56%	6%	4%	6%	nd^{10}
HOMO-2	54%	10%	1%	6%	nd^{10}
HOMO-1	57%	8%	2%	5%	nd^{10}
HOMO	22%	14%	21%	14%	nd^{10}
LUMO	6%	0%	48%	24%	$1D^{10}$
LUMO-1	12%	2%	38%	24%	$1D^{10}$
$IrAu_{24}^{-3}$					
HOMO-7	20%	25%	8%	13%	$1P^{6}$
HOMO-6	25%	32%	1%	13%	$1P^{6}$
HOMO-5	11%	36%	0%	24%	$1P^{6}$
HOMO-4	52%	1%	2%	0%	nd^{10}
HOMO-3	45%	13%	5%	10%	nd^{10}
HOMO-2	54%	5%	0%	5%	nd^{10}
HOMO-1	44%	15%	2%	9%	nd^{10}
HOMO	11%	20%	26%	16%	nd^{10}
LUMO	8%	2%	38%	23%	$1D^{10}$
LUMO-1	9%	2%	36%	25%	$1D^{10}$
Isomer III					
$RhAu_{24}^{-3}$					
HOMO-7	10%	33%	0%	24%	$1P^{6}$
HOMO-6	11%	45%	0%	20%	$1P^{6}$
HOMO-5	2%	55%	0%	22%	$1P^{6}$
HOMO-4	78%	2%	0%	1%	nd^{10}
HOMO-3	22%	12%	25%	11%	nd^{10}
HOMO-2	60%	3%	2%	9%	nd^{10}
HOMO-1	57%	3%	3%	9%	nd^{10}
HOMO	80%	0%	0%	1%	nd^{10}
LUMO	5%	0%	54%	21%	$1D^{10}$
LUMO-1	11%	1%	38%	20%	$1D^{10}$
$IrAu_{24}^{-3}$					
HOMO-7	8%	25%	0%	29%	$1P^{6}$
HOMO-6	17%	39%	0%	20%	$1P^{6}$
HOMO-5	3%	54%	0%	21%	$1P^{6}$
HOMO-4	69%	6%	0%	1%	nd^{10}

HOMO-3	12%	22%	19%	14%	nd[10]
HOMO-2	56%	6%	1%	8%	nd[10]
HOMO-1	49%	0%	8%	18%	nd[10]
HOMO	78%	0%	2%	2%	nd[10]
LUMO	8%	0%	53%	18%	1D[10]
LUMO-1	8%	1%	40%	18%	1D[10]

Table S2. Selected Excited States That Contribute to the Spectra of the Doped Species, Their Energies, Oscillator Strengths and the MO pairs with the Largest Contributions.

Excited State Energy (eV)	Oscillator Strength	Occupied Level	Virtual Level	Peak
$CoAu_{24}^{-3}$				
1.51	0.015	$1P^6$	$1D^4$	A
2.09	0.006	nd^{10}	Au d + thiolate	B
2.11	0.018	$1P^6$	$1D^6$	
2.45	0.045	Au d + thiolate	$1D^4$	C
2.47	0.043	$1P^6$	Au d + thiolate	
2.50	0.029	$1P^6$	Au d + thiolate	
2.77	0.018	nd^{10}	Au d + thiolate	D
2.80	0.023	Au d + thiolate	$1D^4$	
2.91	0.021	Au d + thiolate	$1D^6$	
$RhAu_{24}^{-3}$				
1.65	0.016	$1P^6$	$1D^4$	A
2.14	0.016	$1P^6$	$1D^6$	B
2.22	0.035	$1P^6$	$1D^6$	
2.64	0.042	nd^{10}	1F	C
2.67	0.024	nd^{10}	1F	
2.93	0.035	Au d + thiolate	$1D^4$	D
2.94	0.030	Au d + thiolate	$1D^6$	
$IrAu_{24}^{-3}$				
1.92	0.012	$1P^6$	$1D^4$	A
2.34	0.013	$1P^6$	$1D^6$	B
2.40	0.020	$1P^6$	$1D^6$	
2.63	0.026	nd^{10}	1F	C
2.67	0.011	nd^{10}	1F	
2.76	0.017	Au d + thiolate	$1D^4$	D
2.84	0.019	nd^{10}	1F	
2.89	0.020	nd^{10}	1F	

Table S3. Relative isomer energies and HOMO-LUMO gaps for different isomers of MAu_{24}^{q} systems calculated with SOC. Values in parentheses are results for the scalar-only case.

System	Relative Energies (kcal/mol)[a]			HOMO-LUMO gap (eV)		
	Isomer I	Isomer II	Isomer III	Isomer I	Isomer II	Isomer III
q=-3						
$CoAu_{24}$	0.0(0.0)	39.1(39.0)	-	1.25(1.33)	0.24(0.25)	-
$RhAu_{24}$	0.0(0.0)	34.6(35.9)	41.4(43.3)	1.40(1.55)	0.67(0.71)	0.36(0.61)
$IrAu_{24}$	0.0(0.0)	49.5(50.1)	57.9(59.1)	1.64(1.84)	0.58(0.63)	0.37(0.49)