Supporting Information for

Understanding the Effect of Doping on Energetics and Electronic Structure for Au_{25}, Ag_{25} and Au_{38} Clusters

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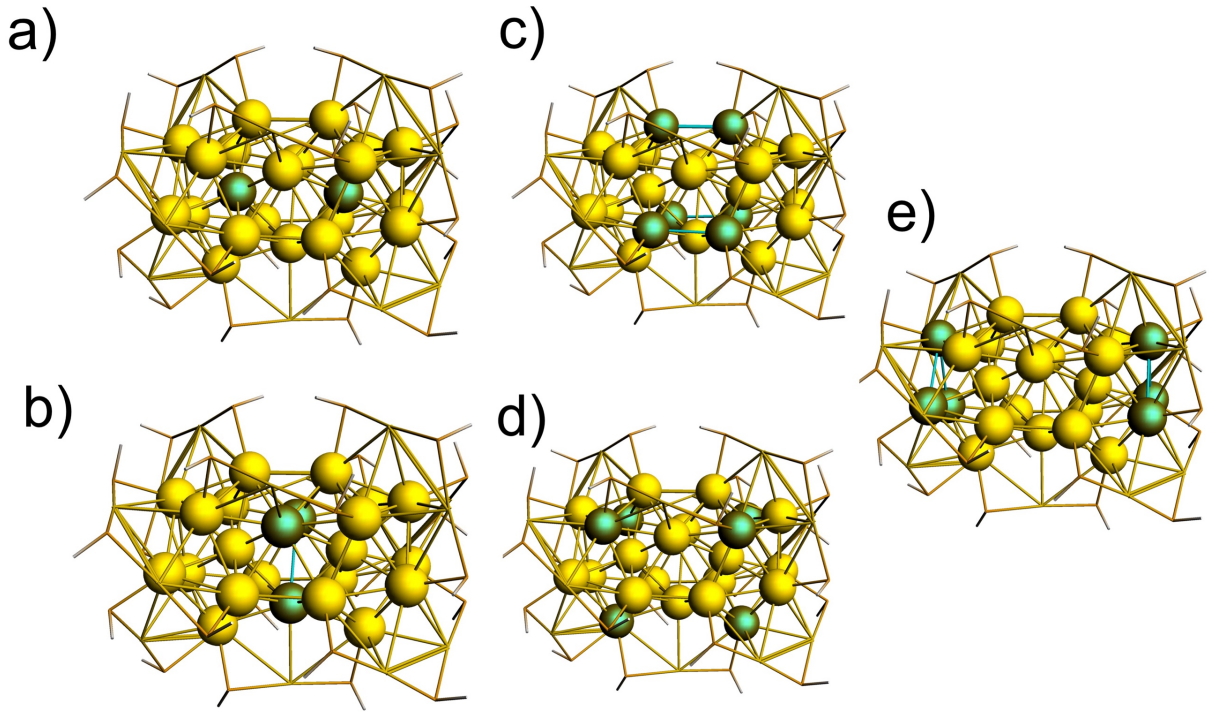

Figure S1. The possible unique positions for dopants in the MAu_{37} cluster. In a) we highlight the dopant positions that result in the isomer I structure whereas b), c), d) and e) show isomer IIa, isomer IIb, isomer IIc, and isomer IId, respectively.

Fragment calculations for the Mulliken population analysis of molecular orbitals in different isomers of MAu_{24}, MAg_{24} and MAu_{37}

In order to understand the interaction between dopant originated atomic orbitals and core-originated super-atomic orbitals, we employ a fragment-type calculation available in ADF for the electronic structure of doped clusters. For this calculation, the doped clusters are divided into three fragments: a) the dopant atom, b) the remaining core (Au_{12}, Ag_{12} or Au_{22}) of the cluster, and c) the ligand shell of the cluster. This fragmentation is illustrated in Figure S2 for an isomer II structure of the MAu_{24} system. In the population analysis for the MOs of the whole cluster, the MOs are defined by the linear combination of MOs of the fragments and atomic orbitals of the dopant (Figure S2). The results are shown in Table S1 for the electronic structure of MAu_{24} systems.

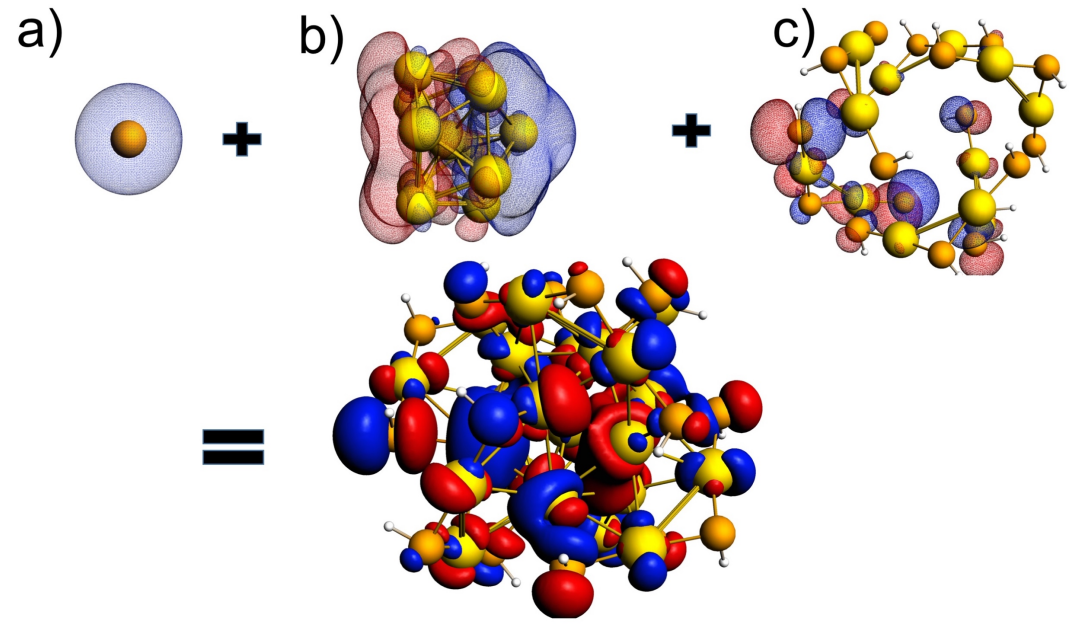

Figure S2. Fragments employed in the population analysis of doped clusters for the isomer II structure. The dopant, core and ligand fragments are illustrated in a, b and c respectively. For this particular MO of the doped cluster, the largest contributions come from a) the s orbital of the dopant and b) the P super-atomic orbital of the core. The resulting MO arises from a bonding interaction between the s and P levels between fragments, and is regarded as the 1P level of the cluster.

Table S1. MO Population Analysis for selected MAu_{24} Systems using Fragment Calculations

MOs	Dopant			Au_{12} core			Au d + thiolate
	s	p	d	S	P	D	
				$AgAu_{24}^{-1}$ Isomer I			
1S	0.18	-	-	0.14	-	-	0.54
1P	-	0.04	-	-	0.49	-	0.41
1P	-	0.04	-	-	0.48	-	0.41
1P	-	0.04	-	-	0.49	-	0.41
1D	-	-	0.01	-	-	0.53	0.36
1D	-	-	0.02	-	-	0.53	0.33
				$AgAu_{24}^{-1}$ Isomer II			
1S	0.03	-	-	0.71	-	-	0.11
1P	0.01	-	-	-	0.46	-	0.37
1P	-	-	0.01	-	0.49	-	0.37
1P	0.04	-	-	-	0.43	-	0.41
1D	-	-	-	-	-	0.53	0.36
1D	-	0.02	-	-	-	0.50	0.33
				$CuAu_{24}^{-1}$ Isomer I			
1S	0.08	-	-	0.45	-	-	0.20
1P	-	0.06	-	-	0.47	-	0.41
1P	-	0.06	-	-	0.47	-	0.41
1P	-	0.06	-	-	0.47	-	0.40
1D	-	-	0.02	-	-	0.55	0.36
1D	-	-	0.02	-	-	0.55	0.33
				$CuAu_{24}^{-1}$ Isomer II			
1S	0.03	-	-	0.72	-	-	0.10
1P	-	-	0.04	-	0.45	-	0.35
1P	-	-	0.07	-	0.43	-	0.32
1P	0.02	0.01	-	-	0.43	-	0.45
1D	-	0.01	-	-	-	0.56	0.28
1D	0.04	0.01	-	-	-	0.50	0.27
				$PtAu_{24}^{-1}$ Isomer I			
1S	0.14	-	-	0.44	-	-	0.35
1P	-	0.04	-	-	0.50	-	0.36
1P	-	0.05	-	-	0.50	-	0.34
1P	-	0.05	-	-	0.50	-	0.36
1D	-	-	0.10	-	-	0.46	0.32
1D	-	-	0.11	-	-	0.46	0.33
				$PtAu_{24}^{-1}$ Isomer II			
1S	0.04	-	-	0.59	-	-	0.20
1P	0.04	-	0.01	-	0.45	-	0.35
1P	-	-	0.19	-	0.37	-	0.31
1P	0.03	-	0.22	-	0.25	0.06	0.29
1D	0.05	0.02	0.02	-	0.03	0.44	0.25
1D	-	-	0.03	-	-	0.53	0.26

$CdAu_{24}^{-1}$ Isomer I							
1S	0.26	-	-	0.43	-	-	0.20
1P	-	0.06	-	-	0.42	-	0.40
1P	-	0.06	-	-	0.43	-	0.38
1P	-	0.05	-	-	0.42	-	0.39
1D	-	-	-	-	-	0.54	0.35
1D	-	-	-	-	-	0.54	0.36
$CdAu_{24}^{-1}$ Isomer II							
1S	0.04	-	0.01	0.59	-	-	0.20
1P	-	-	-	-	0.42	-	0.30
1P	0.06	-	-	-	0.34	-	0.29
1P	-	-	-	-	0.45	0.06	0.31
1D	0.11	0.03	-	-	0.09	0.27	0.31
1D	-	-	-	-	-	0.55	0.30
$InAu_{24}^{-1}$ Isomer I							
1S	0.30	-	-	0.41	-	-	0.24
1P	-	0.09	-	-	0.29	-	0.48
1P	-	0.09	-	-	0.30	-	0.47
1P	-	0.13	-	-	0.30	-	0.46
1D	-	-	-	-	-	0.51	0.39
1D	-	-	-	-	-	0.53	0.40
$InAu_{24}^{-1}$ Isomer II							
1S	0.12	0.03	-	0.66	-	-	0.03
1P	0.12	-	-	-	0.11	-	0.52
1P	0.02	0.01	-	-	0.35	0.01	0.42
1P	-	-	-	-	0.39	-	0.42
1D	0.10	0.07	-	-	0.26	0.05	0.27
1D	-	0.03	-	-	-	0.47	0.27

Table S2. Mulliken Charges and Partial Populations of Group X-XIII Dopants in MAu_{24}^{q} Systems

Isomer	Total Charge	Partial Populations			Isomer	Total Charge	Partial Populations		
		s	p	d			s	p	d
		Ni					Zn		
Isomer I	-0.82	1.27	0.80	8.74	Isomer I	-0.15	0.92	1.24	9.99
Isomer II	0.09	0.45	0.53	8.93	Isomer II	0.45	0.67	0.85	10.03
ΔQ	0.91	-0.82	-0.28	0.19	ΔQ	0.61	-0.26	-0.39	0.03
		Pd					Cd		
Isomer I	-0.28	1.29	-0.26	9.25	Isomer I	-0.33	1.20	1.22	9.91
Isomer II	-0.30	0.78	0.22	9.30	Isomer II	0.35	0.93	0.72	10.00
ΔQ	-0.01	-0.51	0.48	0.05	ΔQ	0.68	-0.26	-0.50	0.09
		Pt					Hg		
Isomer I	-0.76	3.10	6.80	8.86	Isomer I	-0.05	3.14	7.05	9.86
Isomer II	-0.04	2.61	6.43	9.00	Isomer II	0.40	3.06	6.60	9.93
ΔQ	0.72	-0.49	-0.37	0.14	ΔQ	0.45	-0.08	-0.45	0.08
		Cu					Ga		
Isomer I	-0.66	0.91	1.10	9.66	Isomer I	-2.29	1.72	3.46	0.11
Isomer II	0.05	0.48	0.65	9.82	Isomer II	-0.17	1.69	1.38	0.11
ΔQ	0.71	-0.43	-0.44	0.17	ΔQ	2.12	-0.03	-2.08	-0.01
		Ag					In		
Isomer I	-0.67	1.42	0.66	9.59	Isomer I	-1.13	0.98	3.12	0.02
Isomer II	-0.07	0.81	0.46	9.80	Isomer II	0.25	1.42	1.31	0.01
ΔQ	0.60	-0.61	-0.20	0.20	ΔQ	1.38	0.44	-1.81	-0.01
		Au					Tl		
Isomer I	-0.52	3.09	6.92	9.51	Isomer I	-3.02	1.96	4.06	10.00
Isomer II	0.14	2.74	6.49	9.63	Isomer II	-0.03	2.01	1.00	10.02
ΔQ	0.66	-0.35	-0.43	0.12	ΔQ	3.00	0.05	-3.07	0.02

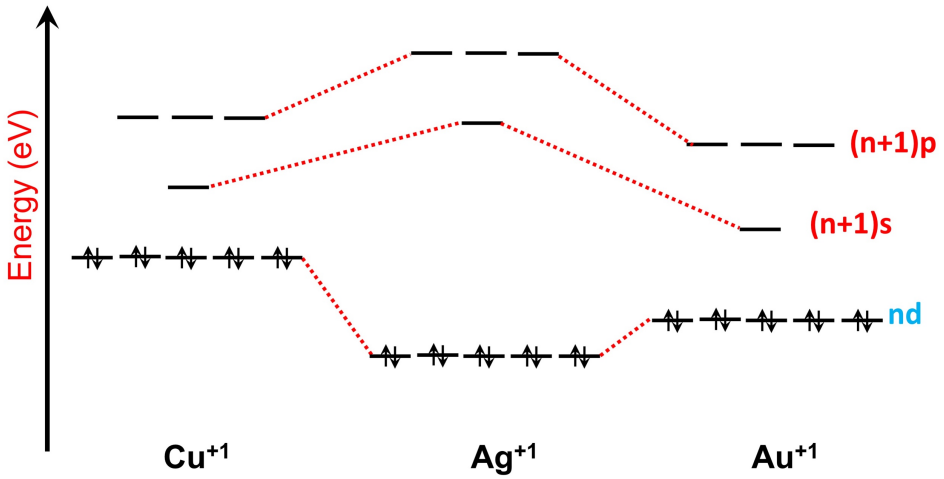

Figure S3. The comparison of valence energy levels for Cu^{+1}, Ag^{+1} and Au^{+1} single atoms calculated with the same level of theory as doped clusters.

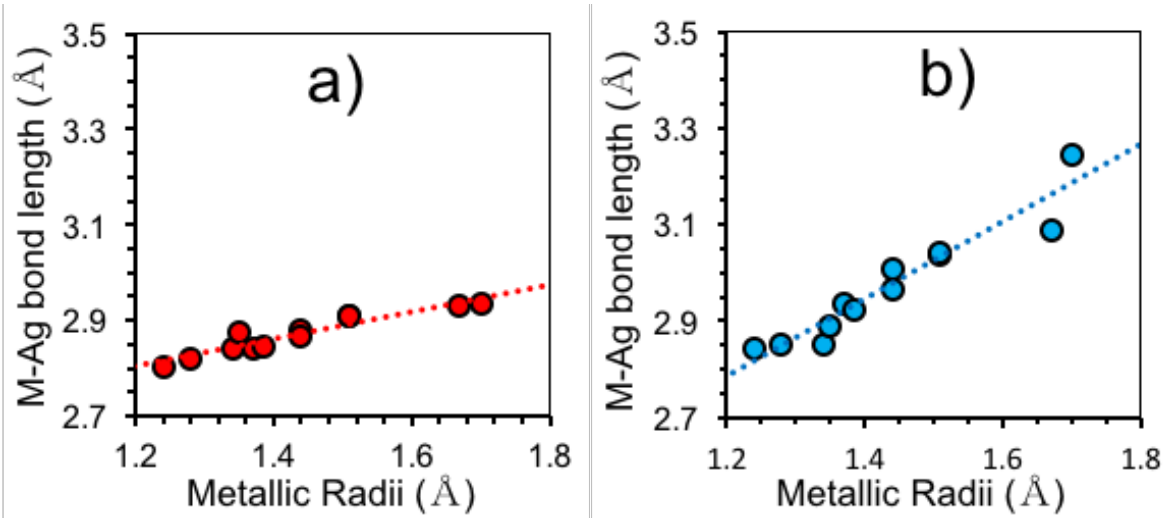

Figure S4. The correlation between metallic radii and M-Ag bond lengths of the MAg_{12} core in doped MAg_{24} clusters for a) isomer I and b) isomer II structures.

Table S3. Mulliken Charges and Partial Populations of Group X-XIII Dopants in MAg_{24}^{q} Systems

Isomer	Total Charge	Partial Populations s	p	d	Isomer	Total Charge	Partial Populations s	p	d
		Ni					Zn		
Isomer I	0.28	0.38	0.53	8.81	Isomer I	0.53	0.48	1.01	9.98
Isomer II	0.19	0.40	0.44	8.96	Isomer II	0.55	0.68	0.76	10.02
ΔQ	-0.09	0.03	-0.09	0.16	ΔQ	0.02	0.20	-0.26	0.04
		Pd					Cd		
Isomer I	0.72	0.11	0.03	9.15	Isomer I	0.22	0.87	1.03	9.88
Isomer II	-0.08	0.54	0.25	9.29	Isomer II	0.42	0.95	0.64	9.98
ΔQ	-0.80	0.43	0.22	0.14	ΔQ	0.20	0.08	-0.39	0.10
		Pt					Hg		
Isomer I	0.18	2.49	6.49	8.84	Isomer I	0.54	2.89	6.79	9.79
Isomer II	0.07	2.57	6.35	9.01	Isomer II	0.50	3.07	6.52	9.92
ΔQ	-0.11	0.09	-0.14	0.17	ΔQ	-0.04	0.18	-0.27	0.12
		Cu					Ga		
Isomer I	0.46	0.06	0.80	9.69	Isomer I	0.54	1.85	0.55	10.06
Isomer II	0.26	0.33	0.58	9.82	Isomer II	0.56	1.70	0.65	10.09
ΔQ	-0.19	0.27	-0.21	0.14	ΔQ	0.02	-0.15	0.11	0.03
		Ag					In		
Isomer I	0.32	0.52	0.59	9.57	Isomer I	1.00	1.44	0.54	10.01
Isomer II	0.06	0.72	0.44	9.78	Isomer II	0.93	1.44	0.62	10.01
ΔQ	-0.26	0.20	-0.15	0.21	ΔQ	-0.08	0.00	0.08	0.00
		Au					Tl		
Isomer I	0.45	2.49	6.62	9.44	Isomer I	-0.05	2.03	1.08	9.94
Isomer II	0.28	2.69	6.42	9.62	Isomer II	0.58	1.87	0.54	10.01
ΔQ	-0.17	0.20	-0.20	0.17	ΔQ	0.62	-0.16	-0.54	0.08

Table S4. Mulliken Charges and Partial Populations of Group X-XIII Dopants in MAu_{37}[(a)] Systems

Isomer	Total Charge	Partial Populations s	p	d	Isomer	Total Charge	Partial Populations s	p	d
		Ni					Zn		
Isomer I	-0.71	1.18	0.76	8.77	Isomer I	0.03	0.83	1.13	10.01
Isomer II	0.05	0.45	0.59	8.90	Isomer II	0.43	0.65	0.89	10.03
ΔQ	0.76	-0.73	-0.17	0.14	ΔQ	0.39	-0.18	-0.24	0.02
		Pd					Cd		
Isomer I	-0.25	1.25	-0.19	9.20	Isomer I	-0.08	1.08	1.07	9.93
Isomer II	-0.29	0.78	0.23	9.29	Isomer II	0.31	0.96	0.76	9.97
ΔQ	-0.04	-0.47	0.42	0.09	ΔQ	0.39	-0.12	-0.31	0.04
		Pt					Hg		
Isomer I	-0.59	3.01	6.74	8.85	Isomer I	0.19	3.02	6.93	9.86
Isomer II	-0.05	2.60	6.46	8.99	Isomer II	0.43	2.96	6.70	9.92
ΔQ	0.54	-0.41	-0.28	0.15	ΔQ	0.24	-0.06	-0.23	0.06
		Cu					Ga		
Isomer I	-0.50	0.81	1.00	9.69	Isomer I	-1.83	1.72	3.00	10.11
Isomer II	-0.01	0.49	0.71	9.81	Isomer II	-0.33	1.70	1.52	10.12
ΔQ	0.50	-0.33	-0.29	0.12	ΔQ	1.50	-0.02	-1.48	0.01
		Ag					In		
Isomer I	-0.53	1.32	0.60	9.61	Isomer I	-0.90	1.03	2.85	10.02
Isomer II	-0.07	0.79	0.48	9.80	Isomer II	0.00	1.20	1.78	10.02
ΔQ	0.46	-0.53	-0.12	0.18	ΔQ	0.89	0.18	-1.06	0.00
		Au					Tl		
Isomer I	-0.33	2.99	6.81	9.53	Isomer I	-1.70	1.76	2.94	10.00
Isomer II	0.13	2.72	6.51	9.64	Isomer II	0.14	2.04	0.80	10.02
ΔQ	0.47	-0.27	-0.30	0.10	ΔQ	1.84	0.28	-2.15	0.02

(a) Tabulated isomer II values are taken from the results of the most stable isomer II structure.

Table S5. Relative Isomer III Energies and HOMO-LUMO Gaps for Doped MAu_{24} and MAg_{24} Systems.

Dopants	MAg_{24} clusters				MAu_{24} clusters			
	Isomer Energies (kcal/mol)		HOMO-LUMO Gap (eV)		Isomer Energies (kcal/mol)		HOMO-LUMO Gap (eV)	
	Isomer I	Isomer III	Isomer I	Isomer III	Isomer I	Isomer III	Isomer I	Isomer III
Group X								
Ni	0.0	19.9	1.25	0.44	0.0	19.5	1.45	0.38
Pd	0.0	11.9	1.28	0.95	0.0	23.2	1.45	0.94
Pt	0.0	26.0	1.56	1.00	0.0	34.1	1.65	1.00
Group XI								
Cu	0.0	-2.4	1.09	1.25	0.0	-0.1	1.41	1.40
Ag or Au	0.0	-12.4	1.06	1.28	0.0	12.7	1.58	1.41
Group XII								
Zn	0.0	-1.3	1.03	0.99	0.0	-5.5	1.51	1.30
Cd	0.0	-6.8	0.99	0.93	0.0	-1.6	1.50	1.21
Hg	0.0	-0.6	1.14	0.81	0.0	11.7	1.64	1.19
Group XIII								
Ga	0.0	11.1	1.18	0.52	0.0	17.5	1.76	0.64
In	0.0	8.1	1.00	0.47	0.0	18.8	1.73	0.66
Tl	0.0	-20.8	1.01	0.67	0.0	17.6	1.74	0.50