Supporting Information

Gold-Caged Metal Clusters with Large HOMO-LUMO Gap and High Electron Affinity

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Figure S1. Nine low-lying and one representative high-energy isomers of Zr@Au_{14} obtained from the combined basin-hopping/DFT global-minimum search. Relative energies are calculated with the BP86/LANL2DZ functional and basis set.

Figure S2. The energy levels of Zr , $D_{2d}\text{-Au}_{14}$, and $D_{2d}\text{-Zr@Au}_{14}$. These levels are calculated with BP86/LANL2DZ functional and basis set.

Table S1. Geometry of $D_{2d}\text{-Zr@Au}_{14}$ and Cartesian co-ordinates using BP86/LANL2DZ, BP86/SDD+Au(2f), PBEPBE/LANL2DZ and PBEPBE/SDD+Au(2f) functionals and basis sets.

Table S2. Geometry of $D_{2d}\text{-Sc@Au}_{14}^-$ and Cartesian co-ordinates using BP86/LANL2DZ, BP86/SDD+Au(2f), PBEPBE/LANL2DZ and PBEPBE/SDD+Au(2f) functionals and basis sets.

Table S3. Geometry of $D_{2d}\text{-Hf@Au}_{14}$ and Cartesian co-ordinates using BP86/LANL2DZ and PBEPBE/LANL2DZ functionals and basis set.

Table S4. Geometry of $D_{2d}\text{-Y@Au}_{14}^-$ and Cartesian co-ordinates using BP86/LANL2DZ and PBEPBE/LANL2DZ functionals and basis set.

Table S5. Harmonic frequencies (IR intensity in parenthesis), HOMO-LUMO gap, and core-shell binding energy of $D_{2d}\text{-Zr@Au}_{14}$ and $D_{2d}\text{-Zr@Ag}_{14}$ with BP86/LANL2DZ functional and basis set.

Table S6: Calculated properties with BP86/LANL2DZ and PBEPBE/LANL2DZ (for Al: 6-31G*) functionals and basis set for $D_{2d}\text{-Zr@Au}_{14}$, $D_{2d}\text{-Hf@Au}_{14}$, $D_{2d}\text{-Sc@Au}_{14}^-$, $D_{2d}\text{-Y@Au}_{14}^-$, $I_h\text{-W@Au}_{12}$, $T_d\text{-Au}_{20}$ and $I_h\text{-Al}_{13}^-$ (Experimental results in parenthesis).

Table S7. Core-shell binding energies (eV) of $D_{2d}\text{-Zr@Au}_{14}$, $D_{2d}\text{-Hf@Au}_{14}$, $D_{2d}\text{-Sc@Au}_{14}^-$, $D_{2d}\text{-Y@Au}_{14}^-$, $I_h\text{-W@Au}_{12}$ and $I_h\text{-Al}_{13}^-$ calculated with BP86/LANL2DZ (For Al: 6-31G(d)) functional and basis set.

Table S8 Calculated EA and experimental EA (or VDE) of the halogen atoms.

Reference 13.

Figure S1. Nine low-lying and one representative high-energy isomers of Zr@Au_{14} obtained from the combined basin-hopping/DFT global-minimum search. Relative energies are calculated with the BP86/LANL2DZ functional and basis set.

Figure S2. The energy levels of Zr, D_{2d} -Au₁₄, and D_{2d} -Zr@Au₁₄. These levels are calculated with BP86/LANL2DZ functional and basis set.

Table S1. Geometry of D_{2d} -Zr@Au₁₄ and Cartesian co-ordinates using BP86/LANL2DZ, BP86/SDD+Au(2f), PBEPBE/LANL2DZ and PBEPBE/SDD+Au(2f) functionals and basis sets.

	BP86/LANL2DZ			PBEPBE/LANL2DZ		
	x	y	z	x	y	z
Au	0.000000	3.038498	0.834394	0.000000	3.033292	0.861111
Au	-1.410112	-2.121271	-1.482329	-1.405622	-2.129416	-1.461755
Au	-1.410112	2.121271	-1.482329	-1.405622	2.129416	-1.461755
Au	2.121271	-1.410112	1.482329	2.129416	-1.405622	1.461755
Au	3.038498	0.000000	-0.834394	3.033292	0.000000	-0.861111
Au	-2.121271	-1.410112	1.482329	-2.129416	-1.405622	1.461755
Au	-3.038498	0.000000	-0.834394	-3.033292	0.000000	-0.861111
Au	2.121271	1.410112	1.482329	2.129416	1.405622	1.461755
Au	-2.121271	1.410112	1.482329	-2.129416	1.405622	1.461755
Au	1.410112	-2.121271	-1.482329	1.405622	-2.129416	-1.461755
Au	0.000000	0.000000	2.818657	0.000000	0.000000	2.803241
Au	0.000000	0.000000	-2.818657	0.000000	0.000000	-2.803241
Au	1.410112	2.121271	-1.482329	1.405622	2.129416	-1.461755
Au	0.000000	-3.038498	0.834394	0.000000	-3.033292	0.861111
Zr	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000

	BP86/SDD+Au(2f)			PBEPBE/ SDD+Au(2f)		
	x	y	z	x	y	z
Au	0.00000	2.98442	0.76284	0.00000	2.97146	0.79908
Au	-1.39773	-2.07901	-1.50661	-1.39143	-2.09611	-1.48663
Au	-1.39773	2.07901	-1.50661	-1.39143	2.09611	-1.48663
Au	2.07901	-1.39773	1.50661	2.09611	-1.39143	1.48663
Au	2.98442	0.00000	-0.76284	2.97146	0.00000	-0.79908
Au	-2.07901	-1.39773	1.50661	-2.09611	-1.39143	1.48663
Au	-2.98442	0.00000	-0.76284	-2.97146	0.00000	-0.79908
Au	2.07901	1.39773	1.50661	2.09611	1.39143	1.48663
Au	-2.07901	1.39773	1.50661	-2.09611	1.39143	1.48663
Au	1.39773	-2.07901	-1.50661	1.39143	-2.09611	-1.48663
Au	0.00000	0.00000	2.82249	0.00000	0.00000	2.80333
Au	0.00000	0.00000	-2.82249	0.00000	0.00000	-2.80333
Au	1.39773	2.07901	-1.50661	1.39143	2.09611	-1.48663
Au	0.00000	-2.98442	0.76284	0.00000	-2.97146	0.79908
Zr	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000

Table S2. Geometry of $D_{2d}\text{-Sc@Au}_{14}^-$ and Cartesian co-ordinates using BP86/LANL2DZ, BP86/SDD+Au(2f), PBEPBE/LANL2DZ and PBEPBE/SDD+Au(2f) functionals and basis sets.

	BP86/LANL2DZ			PBEPBE/LANL2DZ		
	x	y	z	x	y	z
Au	0.000000	3.061299	0.866581	0.000000	3.048358	0.885073
Au	-1.408642	-2.122906	-1.453997	-1.403556	-2.129923	-1.442720
Au	-1.408642	2.122906	-1.453997	-1.403556	2.129923	-1.442720
Au	2.122906	-1.408642	1.453997	2.129923	-1.403556	1.442720
Au	3.061299	0.000000	-0.866581	3.048358	0.000000	-0.885073
Au	-2.122906	-1.408642	1.453997	-2.129923	-1.403556	1.442720
Au	-3.061299	0.000000	-0.866581	-3.048358	0.000000	-0.885073
Au	2.122906	1.408642	1.453997	2.129923	1.403556	1.442720
Au	-2.122906	1.408642	1.453997	-2.129923	1.403556	1.442720
Au	1.408642	-2.122906	-1.453997	1.403556	-2.129923	-1.442720
Au	0.000000	0.000000	2.782670	0.000000	0.000000	2.770928
Au	0.000000	0.000000	-2.782670	0.000000	0.000000	-2.770928
Au	1.408642	2.122906	-1.453997	1.403556	2.129923	-1.442720
Au	0.000000	-3.061299	0.866581	0.000000	-3.048358	0.885073
Sc	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000

	BP86/SDD+Au(2f)			PBEPBE/SDD+Au(2f)		
	x	y	z	x	y	z
Au	0.000000	3.01786	0.81153	0.000000	3.00158	0.84083
Au	-1.39421	-2.08364	-1.45690	-1.38852	-2.09947	-1.44184
Au	-1.39421	2.08364	-1.45690	-1.38852	2.09947	-1.44184
Au	2.08364	-1.39421	1.45690	2.09947	-1.38852	1.44184
Au	3.01786	0.00000	-0.81153	3.00158	0.00000	-0.84083
Au	-2.08364	-1.39421	1.45690	-2.09947	-1.38852	1.44184
Au	-3.01786	0.00000	-0.81153	-3.00158	0.00000	-0.84083
Au	2.08364	1.39421	1.45690	2.09947	1.38852	1.44184
Au	-2.08364	1.39421	1.45690	-2.09947	1.38852	1.44184
Au	1.39421	-2.08364	-1.45690	1.38852	-2.09947	-1.44184
Au	0.000000	0.00000	2.76255	0.000000	0.00000	2.74680
Au	0.000000	0.00000	-2.76255	0.000000	0.00000	-2.74680
Au	1.39421	2.08364	-1.45690	1.38852	2.09947	-1.44184
Au	0.000000	-3.01786	0.81153	0.000000	-3.00158	0.84083
Sc	0.000000	0.00000	0.00000	0.000000	0.00000	0.00000

Table S3. Geometry of D_{2d} -Hf@Au₁₄ and Cartesian co-ordinates using BP86/LANL2DZ and PBEPBE/LANL2DZ functionals and basis set.

	BP86/LANL2DZ			PBEPBE/LANL2DZ		
	x	y	z	x	y	z
Au	0.000000	3.067834	0.862246	0.000000	3.060918	0.861593
Au	-1.406962	-2.109590	-1.448714	-1.403262	-2.107968	-1.444780
Au	-1.405415	2.109317	-1.447363	-1.403262	2.107968	-1.444780
Au	2.109590	-1.406962	1.448714	2.107968	-1.403262	1.444780
Au	3.067834	0.000000	-0.862246	3.060918	0.000000	-0.861593
Au	-2.109317	-1.405415	1.447363	-2.107968	-1.403262	1.444780
Au	-3.067834	0.000000	-0.862246	-3.060918	0.000000	-0.861593
Au	2.109317	1.405415	1.447363	2.107968	1.403262	1.444780
Au	-2.109590	1.406962	1.448714	-2.107968	1.403262	1.444780
Au	1.405415	-2.109317	-1.447363	1.403262	-2.107968	-1.444780
Au	0.000000	0.000000	2.791969	0.000000	0.000000	2.788058
Au	0.000000	0.000000	-2.791969	0.000000	0.000000	-2.788058
Au	1.406962	2.109590	-1.448714	1.403262	2.107968	-1.444780
Au	0.000000	-3.067834	0.862246	0.000000	-3.060918	0.861593
Hf	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000

Table S4. Geometry of D_{2d} -Y@Au₁₄⁻ and Cartesian co-ordinates using BP86/LANL2DZ and PBEPBE/LANL2DZ functionals and basis set.

	BP86/LANL2DZ			PBEPBE/LANL2DZ		
	x	y	z	x	y	z
Au	0.000000	3.020703	0.769260	0.000000	3.020703	0.769260
Au	-1.428312	-2.129394	-1.568866	-1.428312	-2.129394	-1.568866
Au	-1.428312	2.129394	-1.568866	-1.428312	2.129394	-1.568866
Au	2.129394	-1.428312	1.568866	2.129394	-1.428312	1.568866
Au	3.020703	0.000000	-0.769260	3.020703	0.000000	-0.769260
Au	-2.129394	-1.428312	1.568866	-2.129394	-1.428312	1.568866
Au	-3.020703	0.000000	-0.769260	-3.020703	0.000000	-0.769260
Au	2.129394	1.428312	1.568866	2.129394	1.428312	1.568866
Au	-2.129394	1.428312	1.568866	-2.129394	1.428312	1.568866
Au	1.428312	-2.129394	-1.568866	1.428312	-2.129394	-1.568866
Au	0.000000	0.000000	2.909430	0.000000	0.000000	2.909430
Au	0.000000	0.000000	-2.909430	0.000000	0.000000	-2.909430
Au	1.428312	2.129394	-1.568866	1.428312	2.129394	-1.568866
Au	0.000000	-3.020703	0.769260	0.000000	-3.020703	0.769260
Y	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000

Table S5. Harmonic frequencies (IR intensity in parenthesis), HOMO-LUMO gap, and core-shell binding energy of $D_{2d}\text{-Zr@Au}_{14}$ and $D_{2d}\text{-Zr@Ag}_{14}$ with BP86/LANL2DZ functional and basis set.

	$D_{2d}\text{-Zr@Au}_{14}$	$D_{2d}\text{-Zr@Ag}_{14}$
Frequency (cm^{-1})	11.2 (0.0011), 11.2 (0.0011), 21.7 (0.0000), 22.6 (0.0000), 23.3 (0.0007), 23.3 (0.0007), 31.1 (0.0041), 37.5 (0.0000), 43.3 (0.0000), 55.3 (0.0161), 55.3 (0.0161), 62.3 (0.0000), 62.4 (0.0015), 63.4 (0.0023), 63.4 (0.0023), 65.5 (0.0000), 68.9 (0.0000), 69.7 (0.0171), 69.7 (0.0171), 71.5 (0.0000), 80.8 (0.0139), 92.0 (0.0018), 92.9 (0.1951), 92.9 (0.1951), 102.8 (0.0064), 102.8 (0.0064), 106.8 (0.0000), 114.3 (0.0020), 114.3 (0.0020), 118.5 (0.0000), 119.6 (0.0000), 123.1 (0.0000), 126.5 (0.0000), 129.6 (0.0002), 134.0 (0.0313), 134.0 (0.0313), 154.4 (2.2385), 154.4 (2.2385), 192.1 (2.5005)	14.9 (0.0000), 20.9 (0.0000), 37.0 (0.0039), 37.0 (0.0039), 43.6 (0.0846), 43.6 (0.0846), 50.3 (0.0000), 52.8 (0.0135), 52.8 (0.0135), 53.8 (0.0001), 54.9 (0.0005), 70.4 (0.0006), 70.4 (0.0006), 76.6 (0.5196), 76.7 (0.0000), 78.3 (0.0000), 79.6 (0.0010), 79.6 (0.0010), 88.2 (0.0001), 90.5 (0.0000), 96.1 (0.0387), 96.1 (0.0387), 98.8 (0.0000), 117.1 (0.0012), 118.8 (0.2457), 118.8 (0.2457), 123.7 (0.0000), 130.2 (0.0004), 130.2 (0.0004), 139.2 (0.0000), 153.2 (0.0000), 154.3 (0.0000), 155.4 (0.0000), 156.5 (0.0000), 167.2 (0.0006), 167.2 (0.0006), 186.4 (1.8600), 186.4 (1.8600), 224.6 (1.3740)
HOMO-LUMO Gap	2.15 eV	1.84 eV
Core-Shell Binding Energy	13.03 eV	10.23 eV

Table S6: Calculated properties with BP86/LANL2DZ and PBEPBE/LANL2DZ (for Al: 6-31G*) functionals and basis set for D_{2d} -Zr@Au₁₄, D_{2d} -Hf@Au₁₄, D_{2d} -Sc@Au₁₄, D_{2d} -Y@Au₁₄, I_h -W@Au₁₂, T_d -Au₂₀ and I_h -Al₁₃ (Experimental results in parenthesis).

Property	Zr@Au ₁₄	Hf@Au ₁₄	Sc@Au ₁₄	Y@Au ₁₄	W@Au ₁₂	Au ₂₀	Al ₁₃
Symmetry point group	D_{2d}	D_{2d}	D_{2d}	D_{2d}	I_h	T_d	I_h
HOMO/LUMO gap (eV)	2.15/2.15	2.07/2.04	2.04/2.04	1.96/1.96	1.79/1.81 (1.68)^a	1.91/1.88 (1.77)^b	1.85/1.90 (1.4) ^c
Frontier orbital configuration	$(b_1)^2(a_1)^2(e)^4(b_2)^0$	$(b_1)^2(a_1)^2(e)^4(a_1)^0$	$(b_1)^2(a_1)^2(e)^4(a_1)^0$	$(e)^4(a_1)^2(b_2)^0$	$(t_{1u})^6(t_{2g})^6(h_g)^{10}(h_g)^0$	$(t_1)^6(t_2)^6(e)^4(t_2)^0$	$(t_{2u})^6(t_{1u})^6(g_u)^8(h_g)^0$
Vibrational frequency (cm ⁻¹)							
Lowest	11.2/11.4	11.3/10.8	14.7/13.5	6.0/5.4	31.5/33.5	29.2/30.8	73.8/83.5
highest	192.1/198.4	154.0/156.3	227.9/234.3	198.3/198.9	167.3/170.6	172.6/172.2	372.2/383.1
HOMO (eV)	-5.88/-5.71	-5.86/-5.69	-2.58/-2.41	-2.63/-2.47	-5.61/-5.45	-6.02/-5.84	-1.94/-1.91
Au-Au bond length (Å)							
shortest	2.751/2.747	2.748/2.744	2.754/2.748	2.777/2.776	2.921/2.915	2.710/2.714	
longest	2.878/2.883	2.870/2.866	2.873/2.876	2.893/2.893		2.866/2.859	
M-Au bond length (Å)							
shortest	2.819/2.803	2.792/2.788	2.783/2.771	2.909/2.909	2.778/2.772		
longest	2.947/2.940	2.919/2.915	2.933/2.931	3.001/3.006			
VDE (eV)			4.26/4.10	4.25/4.09			3.60/3.58 (3.75)^d

^a ref 6. ^b ref 4. ^c ref 1c. ^d ref 1d.

Table S7. Core-shell binding energies (eV) for $D_{2d}\text{-Zr@Au}_{14}$, $D_{2d}\text{-Hf@Au}_{14}$, $D_{2d}\text{-Sc@Au}_{14}^-$, $D_{2d}\text{-Y@Au}_{14}^-$, $I_h\text{-W@Au}_{12}$ and $I_h\text{-Al@Al}_{12}^-$ clusters, calculated with BP86/LANL2DZ (for Al: 6-31G*) functional and basis set.

Clusters	Core-shell binding energy (eV)
$D_{2d}\text{-Zr@Au}_{14}$	13.03
$D_{2d}\text{-Hf@Au}_{14}$	12.68
$D_{2d}\text{-Sc@Au}_{14}^-$	14.90
$D_{2d}\text{-Y@Au}_{14}^-$	16.09
$I_h\text{-W@Au}_{12}$	11.70
$I_h\text{-Al@Al}_{12}^-$	7.49

Table S8. Calculated EA and experimental EA (or VDE) of the halogen atoms.

Halogen Element	EA (eV)	EA ^c (eV)
F	3.76 ^a	3.40
Cl	3.77 ^a	3.61
Br	3.65 ^a	3.34
I	3.48 ^b	3.06

^a BP86/aug-cc-pVTZ ^b BP86/SDD ^cRef. 19.

Reference 13

Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, (Gaussian, Inc., Wallingford CT, 2004).