Supplementary Information

A new look at the structure of the neutral Au_{18} cluster: Hollow versus filled golden cage

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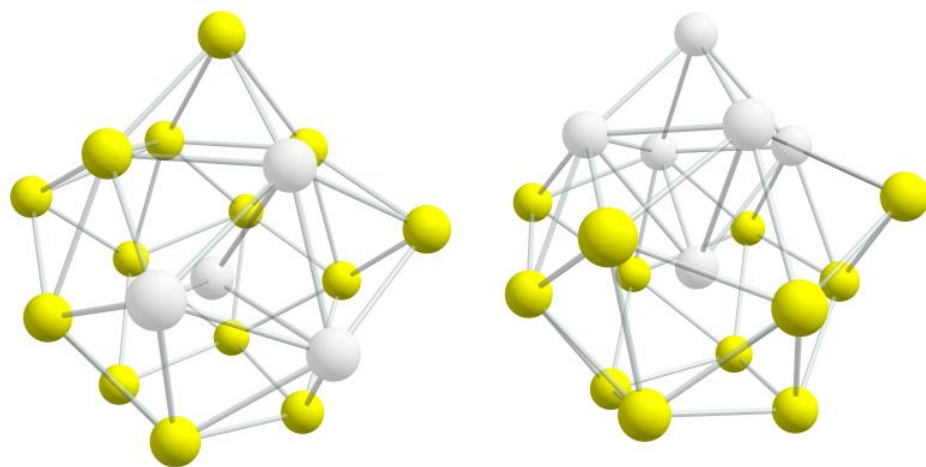[f] Institute for Computational Science and Technology (ICST), Ho Chi Minh City, Vietnam. Email: tho.nm@icst.org.vn

Figure S1. Distorted tetrahedral Au$_4$ (left) and octahedral Au$_6$ (right) units found in **18_1** isomer.
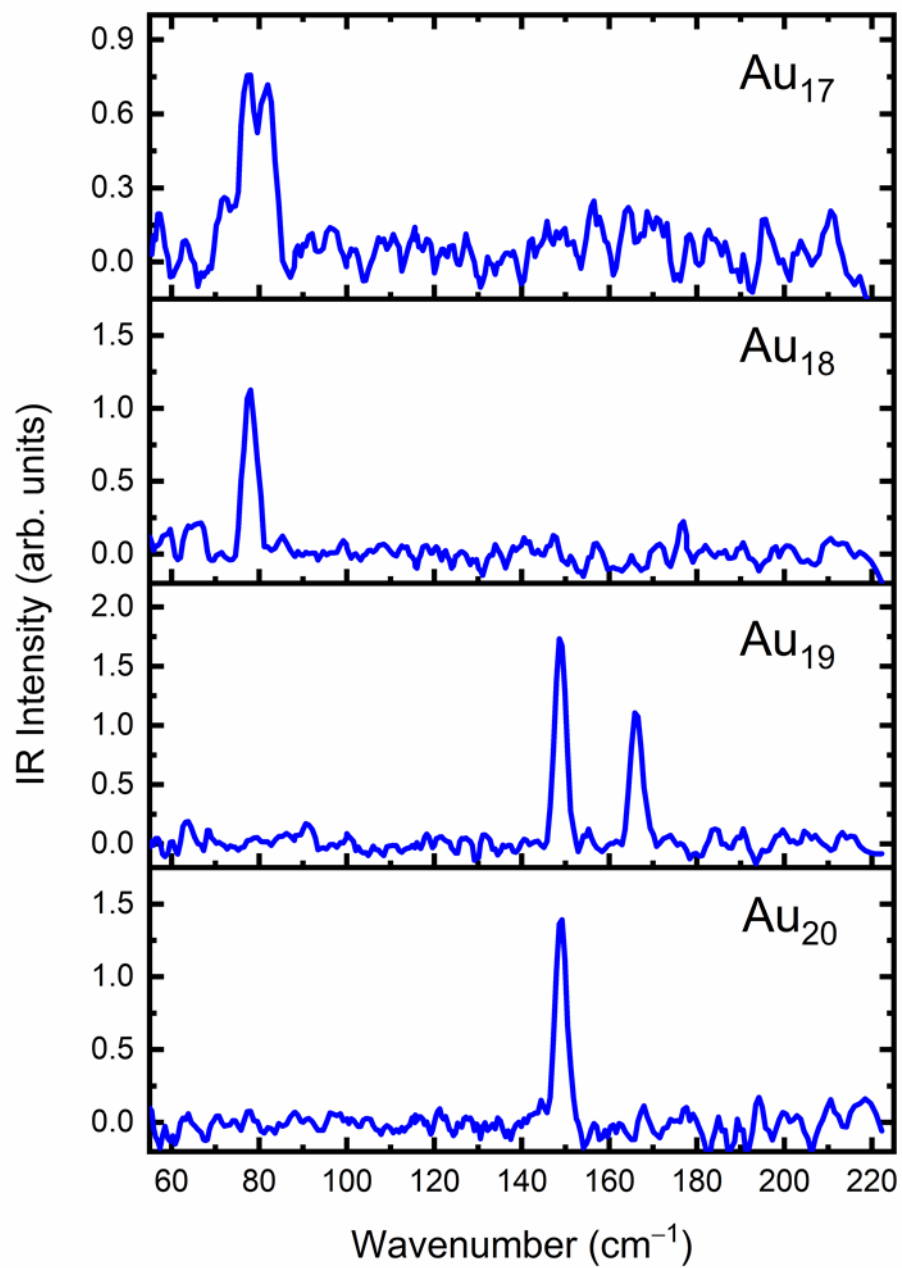
Figure S2. Experimental FIR-MPD of Au_n-Kr (n = 17 – 20) clusters.

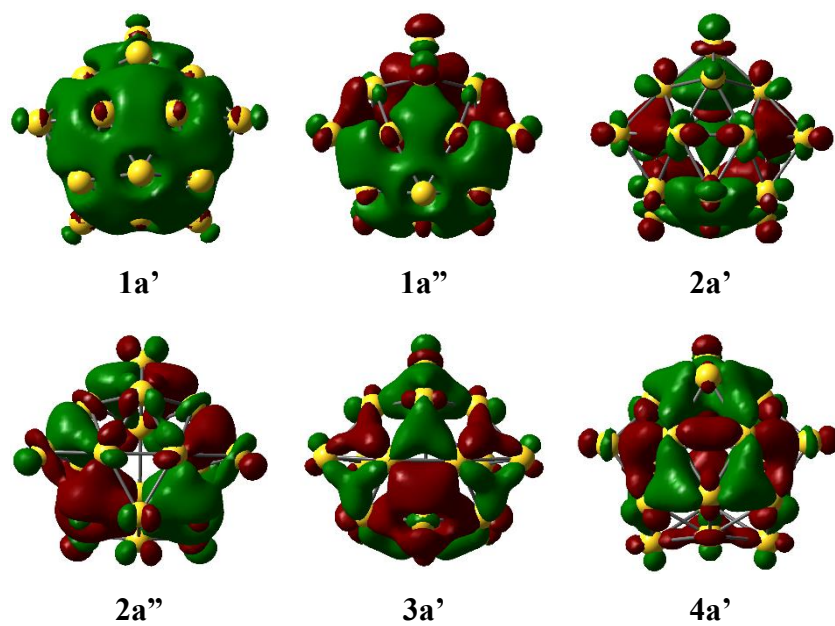**1a'** **1a"** **2a'**

2a" **3a'** **4a'**

Figure S3. Shapes of orbitals in **18_5** formed from orbital interactions between the Au$_{17}$ framework and the exohedral Au atom.
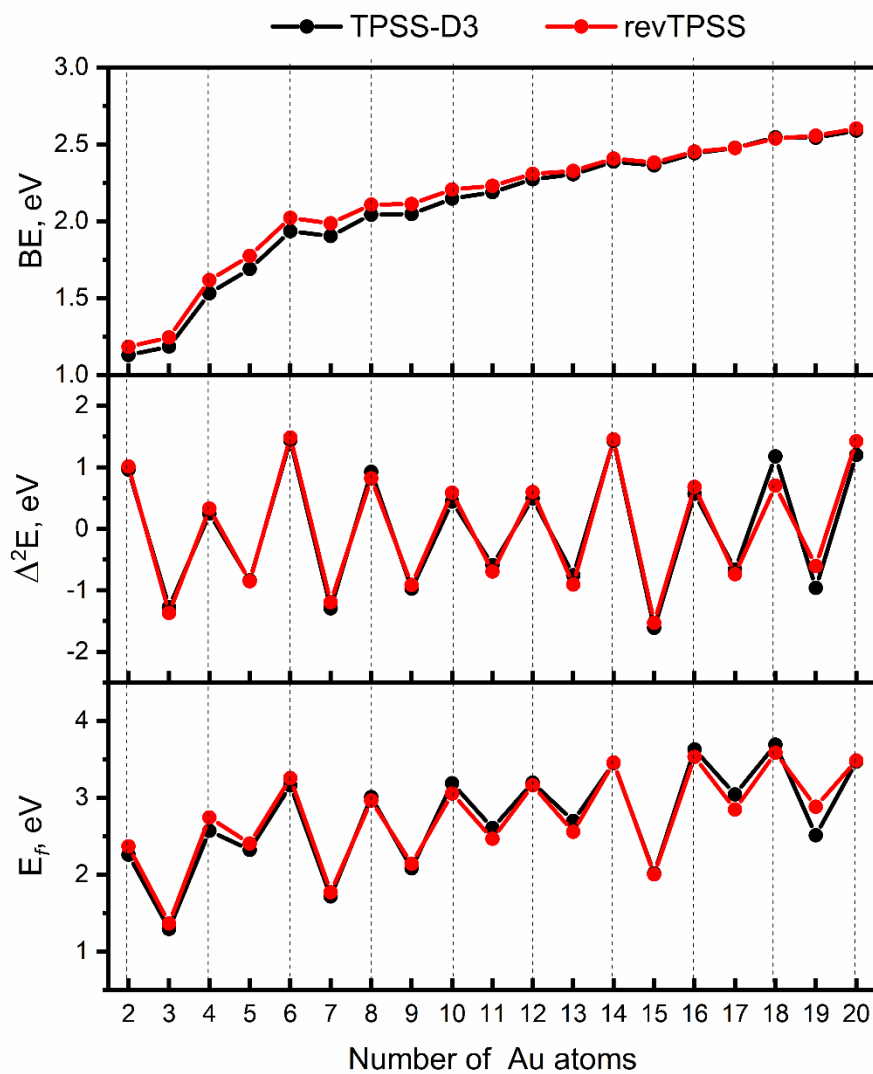
Figure S4. Binding energies per atom (E_b), one-step fragmentation energies (E_f) and second-order difference of energy ($\Delta^2 E$) for neutral Au_n clusters as a function of cluster size. Results are obtained using both revTPSS and TPSS-D3 functionals.
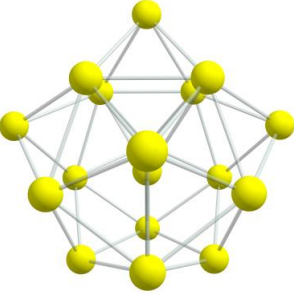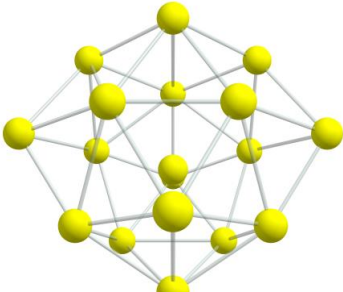
Table S1. Vibrational frequencies (cm^{-1}) of the most intense peaks in some small Au_n clusters at their equilibrium structures, computed with different functionals in comparison with experimental data.
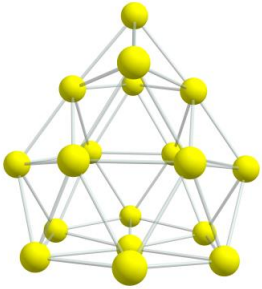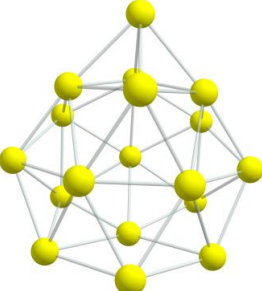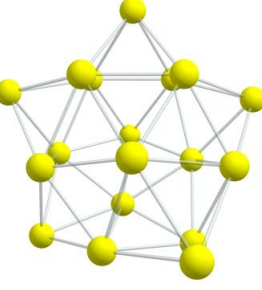
Method	Au_2	Au_7			Au_{19}		Au_{20}	RMSD[b]
PW91	173	155	175	188	135	152	137	13.2
PBE	172	154	174	186	135	153	136	13.9
B3LYP	166	145	163	177	122	144	125	23.5
BLYP	161	142	159	173	118	143	122	27.0
TPSS	178	159	180	193	144	160	144	7.4
TPSS-D3	176	158	179	192	141	160	142	8.8
Experiment[a]	191	165	186	201	149	166	148	-

[a] Taken from ref. S1. Value for Au_2 is taken from ref. S2

[b] Root-mean-square deviations from experimental values.

Table S2. Low-lying isomers of the Au$_{18}$ cluster and their Cartesian coordinates (in Å) located using TPSS-D3/aVDZ-PP geometry optimizations.

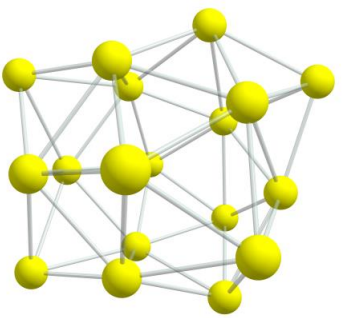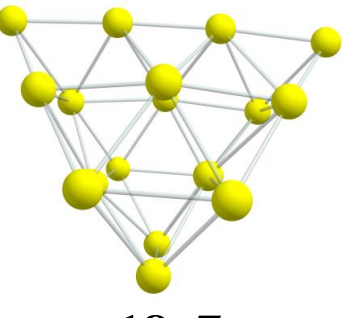| Isomer	Cartesian coordinates		
18_1	79	0.256660000	-0.000797000	3.150669000
	79	-0.738454000	-2.224518000	-1.838007000
	79	0.837817000	3.504424000	0.000000000
	79	1.882760000	1.386305000	1.423766000
	79	-0.720336000	2.231336000	1.837811000
	79	1.872302000	-1.402836000	-1.423390000
	79	1.872302000	-1.402836000	1.423390000
	79	0.807599000	-3.512146000	0.000000000
	79	-2.358513000	0.009984000	2.106820000
	79	-0.738454000	-2.224518000	1.838007000
	79	3.765549000	-0.014318000	0.000000000
	79	-2.358513000	0.009984000	-2.106820000
	79	0.256660000	-0.000797000	-3.150669000
	79	-0.720336000	2.231336000	-1.837811000
	79	-2.719689000	-1.745261000	0.000000000
	79	-2.704910000	1.768114000	0.000000000
	79	1.882760000	1.386305000	-1.423766000
	79	-0.375205000	0.000238000	0.000000000
18_2	79	3.220200000	-0.930680000	0.000000000
	79	0.387282000	0.076152000	0.000000000
	79	-0.108900000	1.737709000	2.300167000
	79	2.493105000	1.325983000	-1.477793000
	79	0.750236000	2.918239000	0.000000000
	79	1.612744000	-1.242446000	2.229571000
	79	1.077618000	-2.767320000	0.000000000
	79	2.493105000	1.325983000	1.477793000
	79	-0.510924000	-0.618219000	3.746494000
	79	-1.125572000	-1.866824000	-1.393695000
	79	-0.108900000	1.737709000	-2.300167000
	79	-1.125572000	-1.866824000	1.393695000
	79	1.612744000	-1.242446000	-2.229571000
	79	-0.510924000	-0.618219000	-3.746494000
	79	-3.243486000	-0.795171000	0.000000000
	79	-1.833886000	1.840575000	0.000000000
	79	-2.539435000	0.492899000	-2.272614000
	79	-2.539435000	0.492899000	2.272614000
	79	-1.972593000	1.384024000	0.289269000
	79	1.393290000	-2.380523000	-2.205929000
	79	1.972593000	-1.384024000	0.289269000
	79	0.000000000	-1.731438000	2.197396000
	79	-1.393290000	-2.380523000	-2.205929000

	79	-1.972593000	-1.384024000	0.289269000
	79	-2.157789000	0.000000000	2.615069000
	79	2.731666000	0.000000000	-1.981623000
	79	-1.393290000	2.380523000	-2.205929000
	79	-2.731666000	0.000000000	-1.981623000
	79	0.000000000	1.731438000	2.197396000
	79	0.000000000	3.275468000	0.003706000
	79	2.157789000	0.000000000	2.615069000
18_3	79	0.000000000	-3.275468000	0.003706000
	79	0.000000000	0.000000000	-2.329379000
	79	1.393290000	2.380523000	-2.205929000
	79	1.972593000	1.384024000	0.289269000
	79	0.000000000	0.000000000	4.326925000

	79	-0.187964000	-0.136867000	3.423670000
	79	-0.187964000	-0.136867000	-3.423670000
	79	-0.612618000	2.006873000	1.864402000
	79	-0.612618000	2.006873000	-1.864402000
	79	-0.817819000	4.005404000	0.000000000
	79	-1.961743000	-0.374375000	1.363197000
	79	-2.624718000	1.871318000	0.000000000
	79	-1.961743000	-0.374375000	-1.363197000
	79	-0.652004000	-2.608443000	-2.354984000
18_4	79	-2.033279000	-2.779988000	0.000000000
	79	-0.652004000	-2.608443000	2.354984000
	79	1.428718000	2.450499000	0.000000000
	79	1.989625000	1.197021000	2.353523000
	79	1.989625000	1.197021000	-2.353523000
	79	0.755173000	-2.432970000	0.000000000
	79	2.304186000	-0.147550000	0.000000000
	79	1.918574000	-1.567565000	2.287200000
	79	1.918574000	-1.567565000	-2.287200000

	79	-0.434786000	-2.862584000	0.000000000
	79	1.531562000	3.788108000	0.000000000
	79	1.386799000	-0.296271000	2.267128000
	79	1.186141000	-3.031325000	-2.201280000
	79	2.058477000	-1.594537000	0.000000000
	79	-1.183180000	-1.583880000	2.273479000
	79	-2.715622000	-1.358128000	0.000000000
	79	1.186141000	-3.031325000	2.201280000
18_5	79	-0.742745000	0.639482000	3.809093000
	79	-1.860870000	0.889565000	-1.335677000
	79	1.386799000	-0.296271000	-2.267128000
	79	-1.860870000	0.889565000	1.335677000
	79	-1.183180000	-1.583880000	-2.273479000
	79	-0.742745000	0.639482000	-3.809093000
	79	-1.185037000	3.148162000	0.000000000

	79	2.056649000	1.103473000	0.000000000
	79	0.558234000	2.270182000	-2.030978000
	79	0.558234000	2.270182000	2.030978000
18_6	79	0.114121000	-0.423473000	3.120924000
	79	-1.875539000	-1.299728000	-1.428727000
	79	2.780466000	1.954571000	0.000000000
	79	2.248897000	-0.295758000	1.413560000
	79	0.688566000	1.900425000	1.849055000
	79	0.583286000	-2.488523000	-1.413798000
	79	0.583286000	-2.488523000	1.413798000
	79	-1.526168000	-3.574069000	0.000000000
	79	-1.953836000	1.235134000	2.350974000
	79	-1.875539000	-1.299728000	1.428727000
	79	2.932172000	-2.555842000	0.000000000
	79	-1.953836000	1.235134000	-2.350974000
	79	0.114121000	-0.423473000	-3.120924000
	79	0.688566000	1.900425000	-1.849055000
	79	-3.297934000	0.543447000	0.000000000
	79	-1.348935000	2.435694000	0.000000000
	79	2.248897000	-0.295758000	-1.413560000
	79	0.849407000	3.940044000	0.000000000
18_7	79	3.318086000	-0.164022000	1.371145000
	79	1.235884000	-1.454442000	2.678568000
	79	-0.804886000	-2.677792000	1.476071000
	79	-0.804886000	-2.677792000	-1.476071000
	79	1.235884000	-1.454442000	-2.678568000
	79	3.318086000	-0.164022000	-1.371145000
	79	1.433704000	-1.762855000	0.000000000
	79	1.446464000	1.372646000	2.696438000
	79	1.219617000	1.181532000	0.000000000
	79	1.446464000	1.372646000	-2.696438000
	79	-0.919167000	0.068561000	1.785377000
	79	-2.687221000	-1.131340000	0.000000000
	79	-0.919167000	0.068561000	-1.785377000
	79	-0.530618000	2.783836000	-1.568850000
	79	-0.530618000	2.783836000	1.568850000
	79	-2.532776000	1.496187000	0.000000000
	79	-2.737123000	-3.828175000	0.000000000
	79	-2.187726000	4.187077000	0.000000000

References

S1. P. Gruene, D. M. Rayner, B. Redlich, A. F. van der Meer, J. T. Lyon, G. Meijer and A. Fielicke, *Science*, 2008, **321**, 674-676.

S2. M. D. Morse, *Chem. Rev.*, 1986, **86**, 1049-1109.