Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Superatom-atom super-bonding in metallic clusters: A new look to the mystery of Au_{20} pyramid

by

Longjiu Cheng[1]*, Xiuzhen Zhang[1], Baokang Jin[1], and Jinlong Yang[2]*

[1]Department of Chemistry, Anhui University, Hefei, Anhui, 230039, People's Republic of China.

[2]Hefei National Laboratory for Physics Sciences at the Microscale, University of Science & Technology of China, Hefei, Anhui, 230026, People's Republic of China.

*Corresponding authors. E-mail: clj@ustc.edu (L.C.); jlyang@ustc.edu.cn (J.Y.)

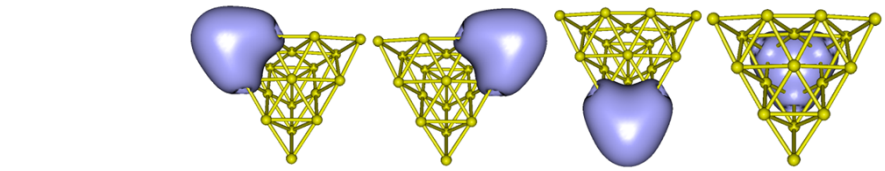
Computational details:

Geometries of Au_{20} and TX_4 are relaxed by density functional theory (DFT) calculations performed on the Gaussian 09 package.[s1] DFT geometry relaxations are performed using the TPSS method with the LANL2DZ basis set for Au element (TPSS/LANL2DZ). Natural bonding analysis by AdNDP is also performed at the same TPSS/LANL2DZ level of theory. For OsH_4 and $OsCl_4$, all the calculations performed on the TPSS functional with LANL2DZ basis set for Os and 6-31G* for Cl and H. Molecular orbital (MO) visualization is performed using MOLEKEL 5.4 software.[s2] The reaction energies of $4/5\ Au_{20} + 2\ X_2 \rightarrow TX_4$ are calculated in TPSS/Def2tzvp/6-311G** level of theory.

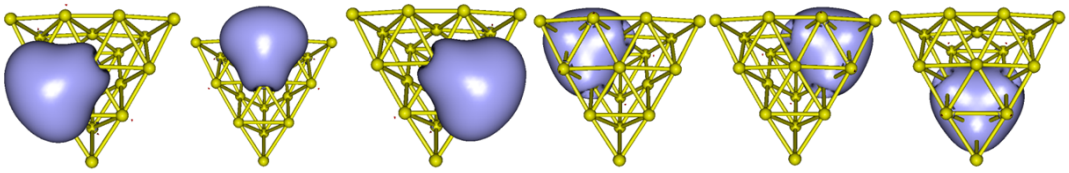
REFERENCES

(s1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, Jr., J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian 09, revision B.01; Gaussian, Inc., Wallingford CT (2009).

(s2) Varetto, U.; Molekel 5.4.0.8, Swiss National Supercomputing Centre, Manno (Switzerland).



4 × 4c-2e bond ON = 1.84 |e|



6 × 4c-2e bond ON = 1.69 |e|

Figure S1. AdNDP localized natural bonding orbitals of ten 4c-2e bonds of Au_{20} (T_d) at TPSS/Lanl2DZ level of theory. ON gives the occupancy numbers. The ON numbers are also 1.84 |e| and 1.69 |e| at B3PW91/Lanl2DZ level of theory as in [J. Phys. Chem. A 2009, 113, 866–868].

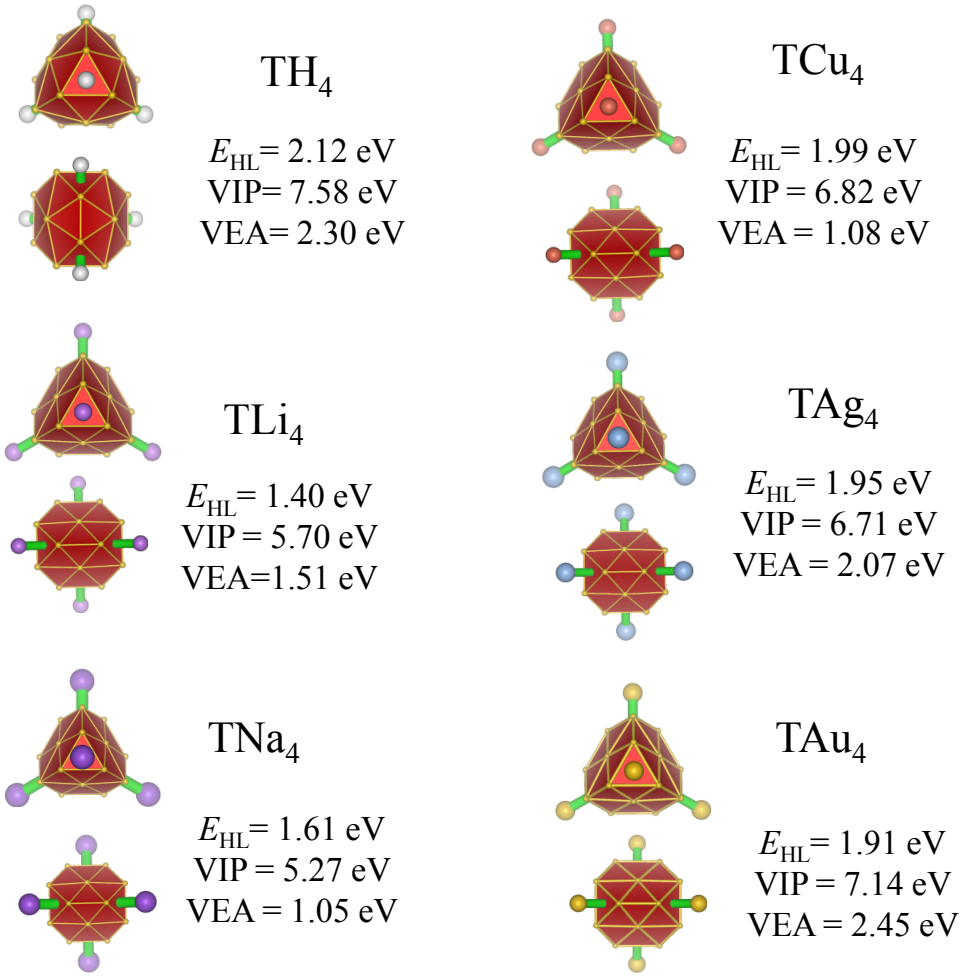


Figure S2. Structures of $Au_{16}M_4$ (TM_4, M=H, Li, Na, Cu, Ag, Au) at TPSS/def2tzvp/6-311G** level. E_{HL}: HUMO-LUMO gaps; VIP: vertical ionic potential; VEA: vertical electron affinity.

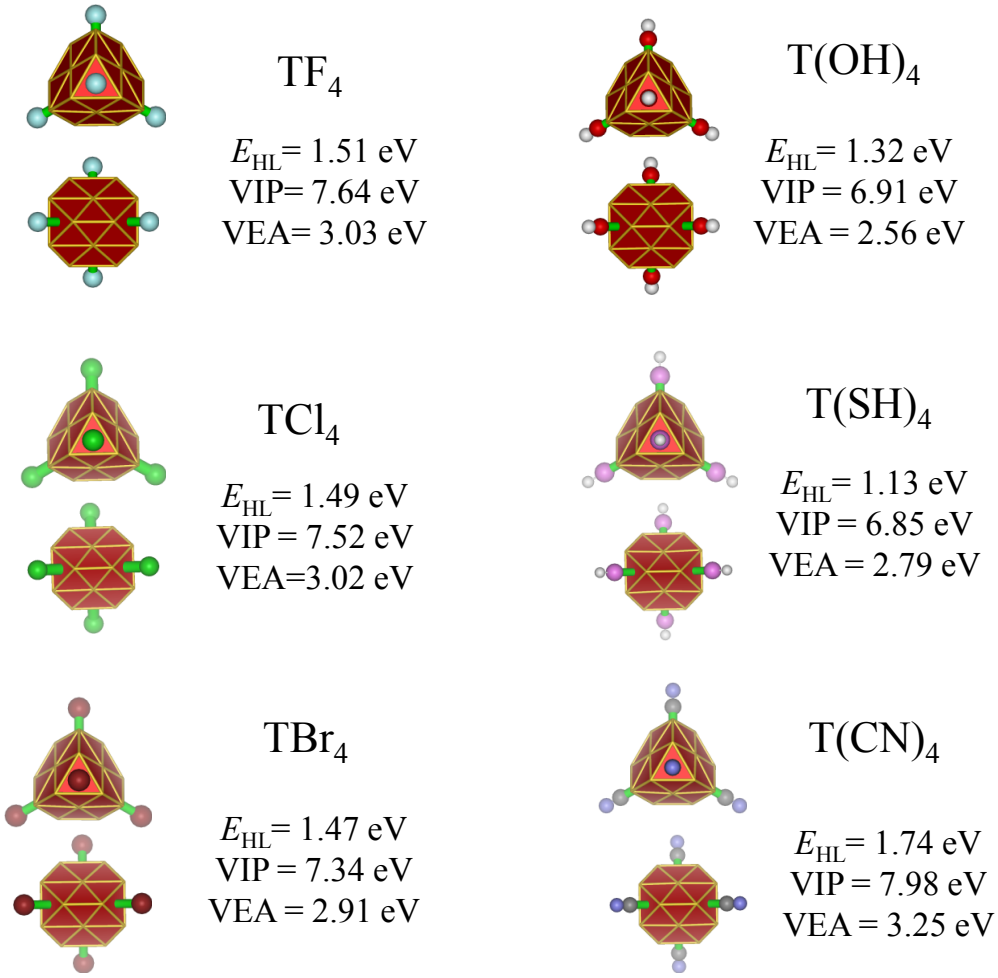


Figure S3. Structures of $Au_{16}X_4$ (TX_4, M=F, Cl, Br, OH, SH, CN) at TPSS/def2tzvp/6-311G** level. E_{HL}: HUMO-LUMO gaps; VIP: vertical ionic potential; VEA: vertical electron affinity.

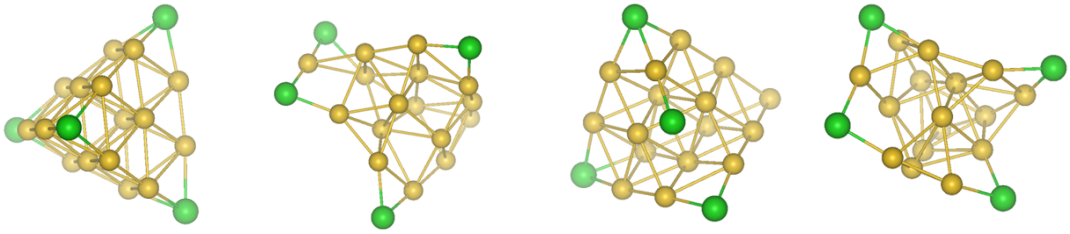


Figure S4. Structures of the low-energy isomers of $Au_{16}Cl_4$ clusters at the TPSS/LANL2DZ/6-31G* level of theory. The structures are located by unbiased global search using genetic algorithm plus DFT.

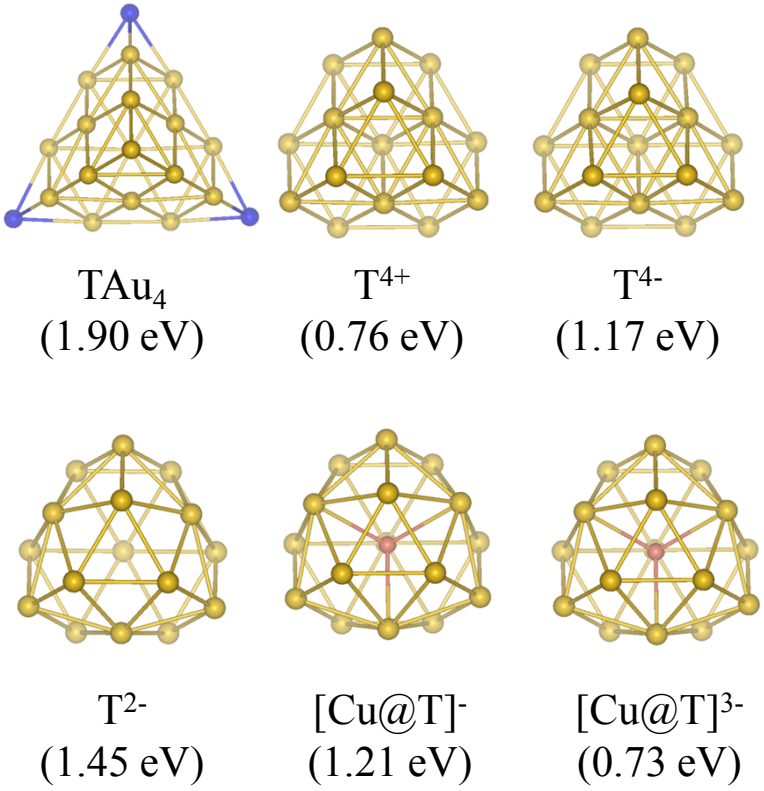


Figure S5. Optimized structures of TAu_4, T^{4+}, T^{4-}, T^{2-}, $[Cu@T]^-$, and $[Cu@T]^{3-}$ at the TPSS/LANL2DZ level of theory. Enclosed are the HOMO-LUMO gaps in eV.