Supporting Information

Cubic Aromaticity in Octahedral $NbTcAu_4$ Featuring a Stable Nb-Tc Quadruple Bond plus four additional delocalized interactions

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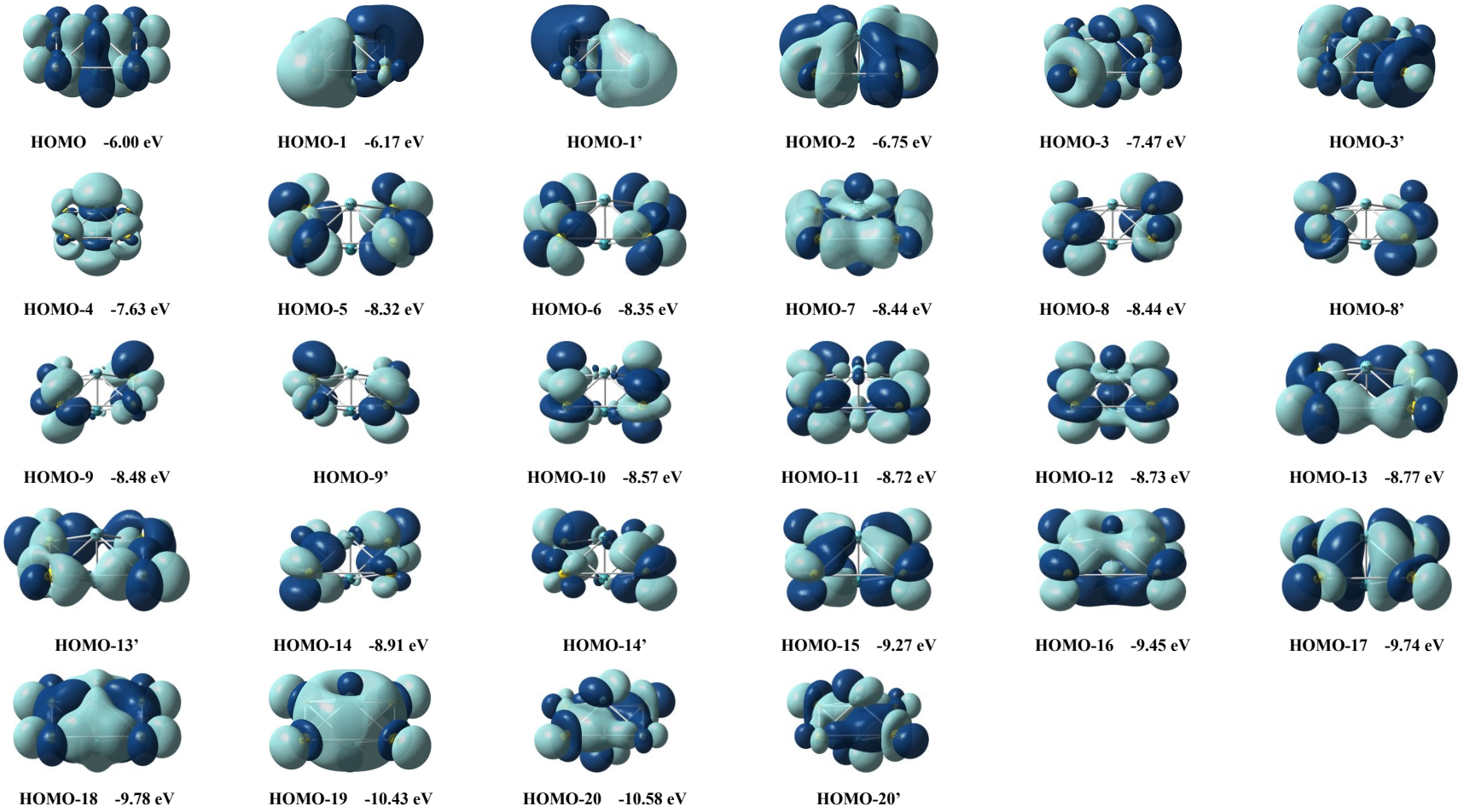

Figure S1. Valence canonical molecular orbital contours for the C_{4v}-$NbTcAu_4$ structure at the PBE0/Def2-TZVP level. (Isovalue density = 0.02)

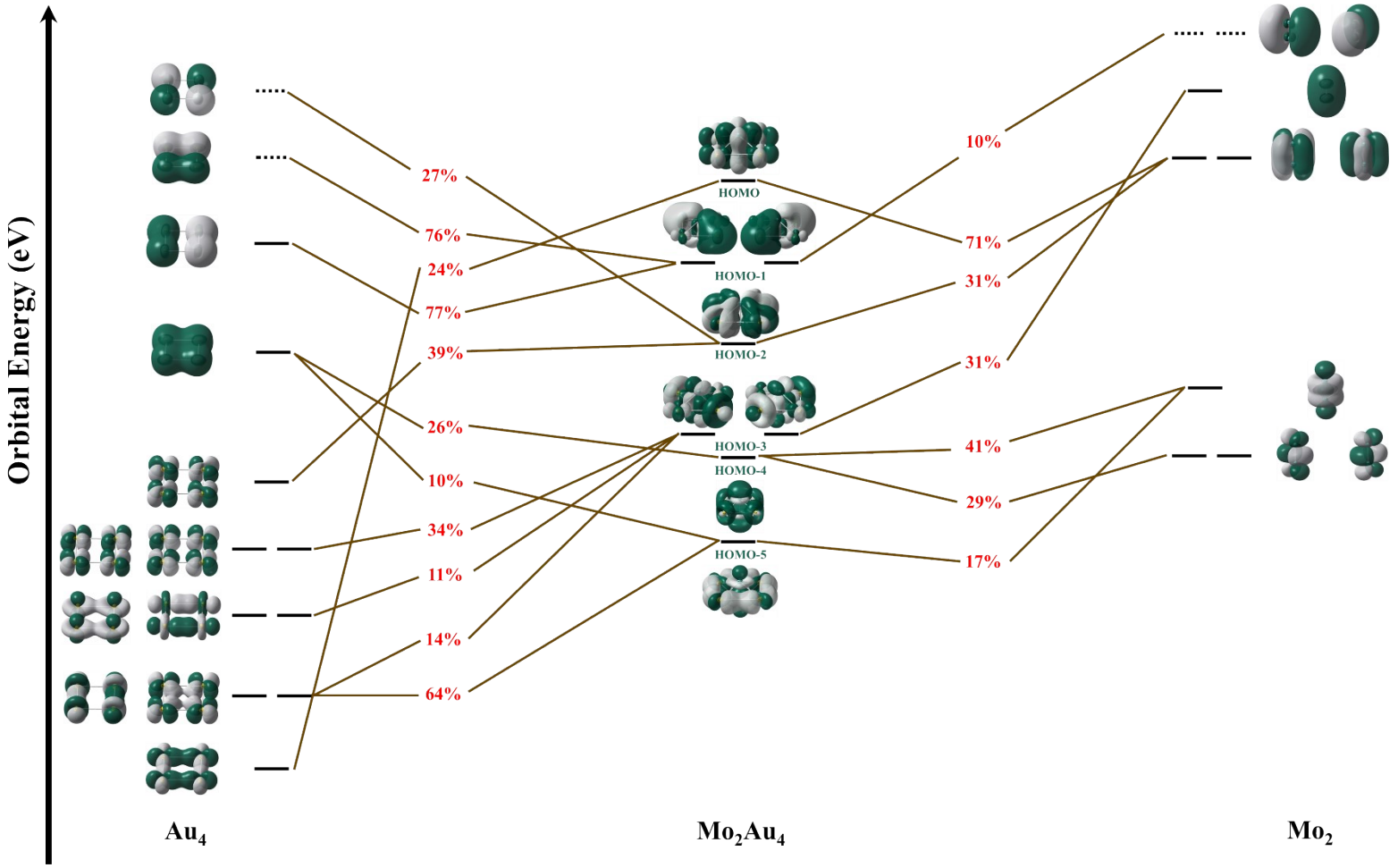

Figure S2. Qualitative orbital correlation diagram of the interactions between the $D_{\infty h}$-Mo_2 fragment and the C_{4v}-Au_4 fragment in the C_{4v}-Mo_2Au_4. The horizontal dashed and solid lines represent virtual and occupied molecular orbitals, respectively.

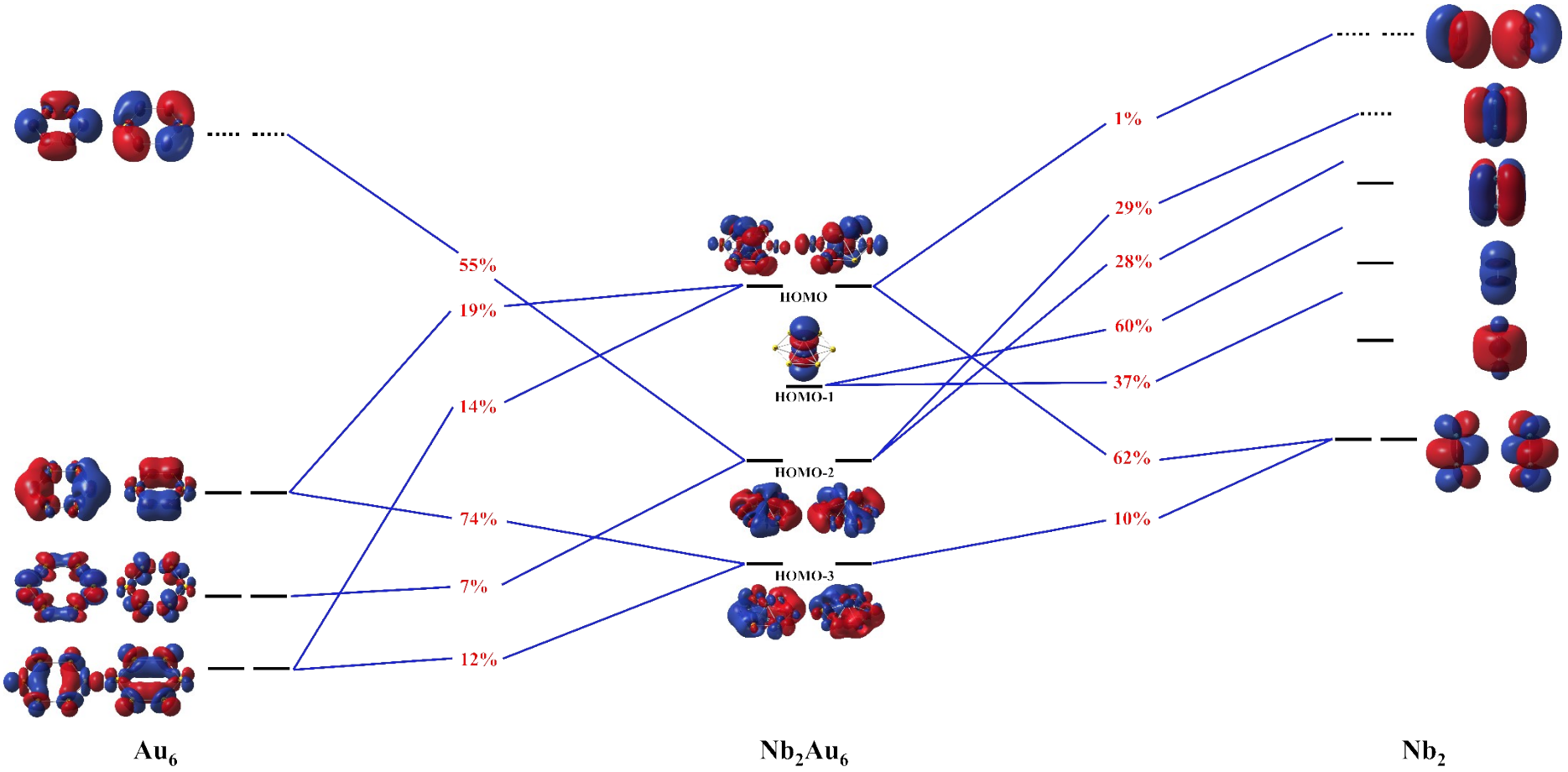

Figure S3. Qualitative orbital correlation diagram of the interactions between the $D_{\infty h}$-Nb_2 fragment and the D_{6h}-Au_6 fragment in the D_{6h}- Nb_2Au_6. The horizontal dashed and solid lines represent virtual and occupied molecular orbitals, respectively.

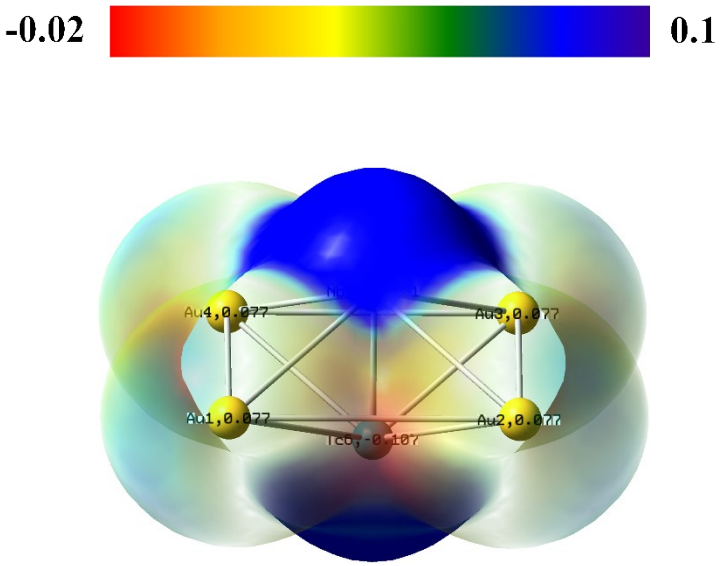

Figure S4. The electrostatic potential on the molecular surface of C_{4v}-$NbTcAu_4$. (Isoval Density = 0.01)

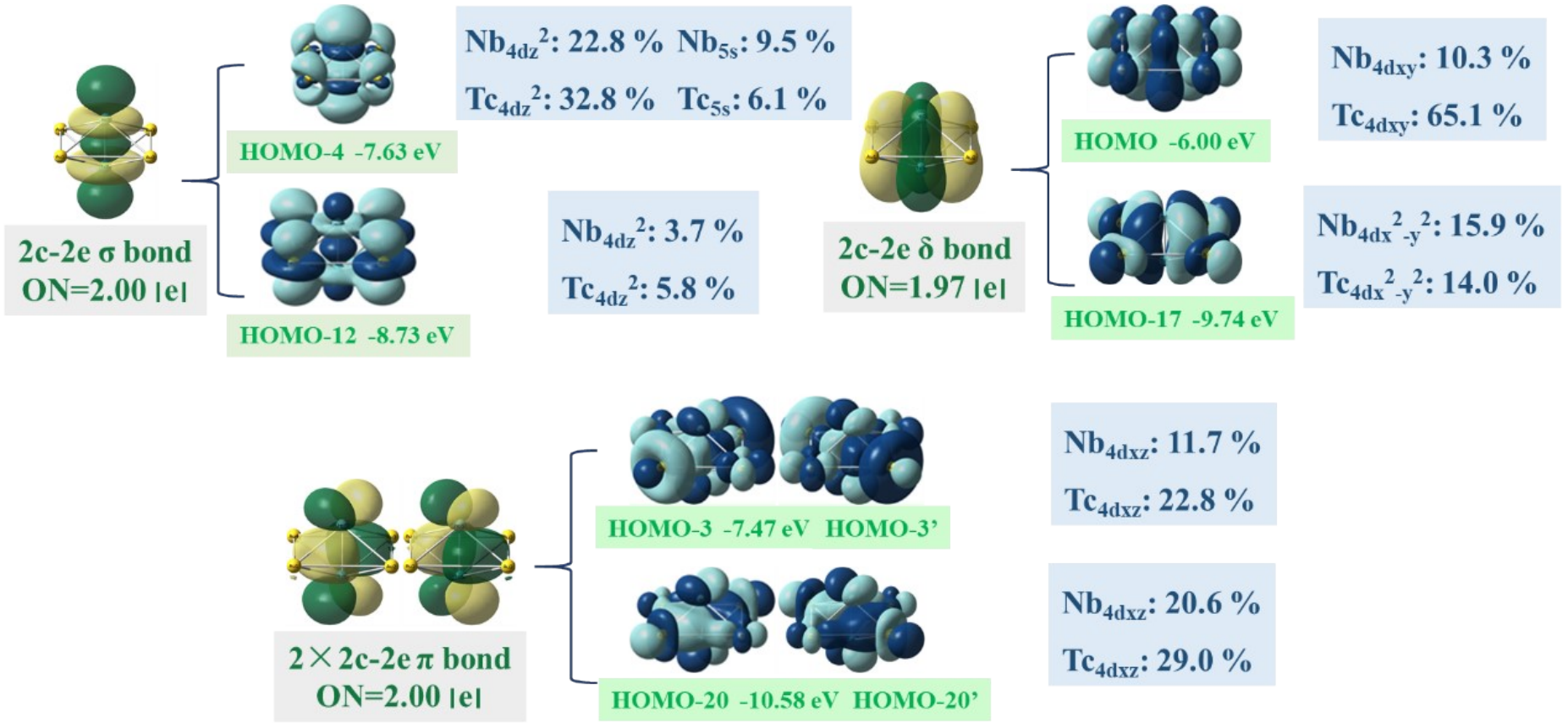

Figure S5. Composition analysis of molecular orbitals corresponding to the 2c-2e Nb-Tc bonding orbitals identified by AdNDP.

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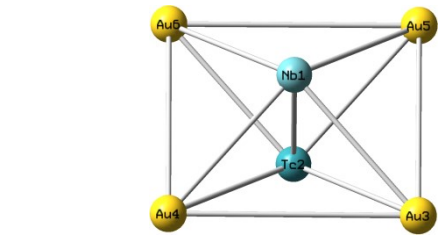
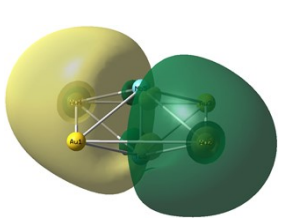
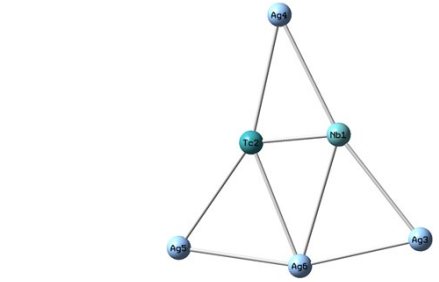
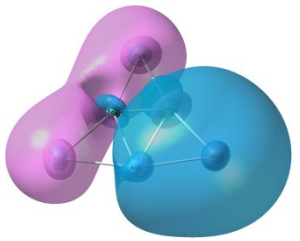
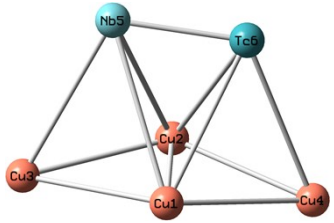
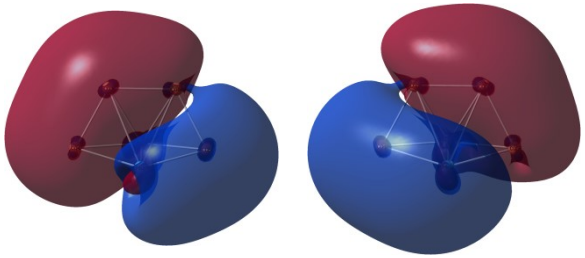
NbTc						
	$Nb©5p_y$~16.3%	$Nb©5p_x$~16.3%	$Nb©5p_x$~8.5%	$Nb©5p_x$~4.2%	$Nb©5p_y$~3.9%	$Nb©5p_x$~3.3%
	$Tc©5p_y$~14.3%	$Tc©5p_x$~14.3%	$Tc©5p_x$~1.2%	$Tc©5p_x$~4.6%	$Tc©5p_y$~19.7%	$Tc©5p_x$~19.9%

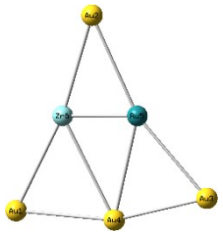
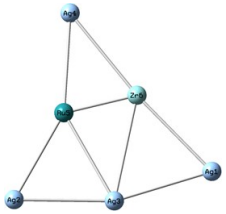
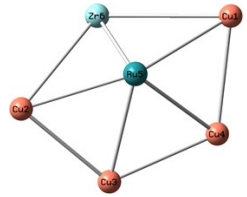
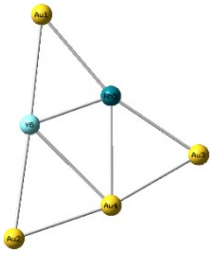
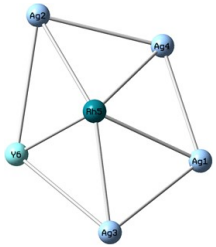
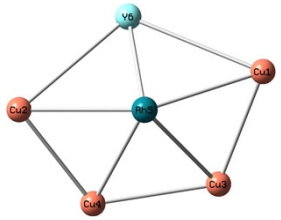
	Au_4		Ag_4		Cu_4	
ZrRu						
	$Zr©5p_x$~3.2%	$Zr©5p_y$~3.1%	$Zr©5p_x$~1.5%	Zr©5px~1.5%	$Zr©5p_y$~2.0%	$Zr©5p_x$~2.0%
	$Ru©5p_x$~1.3%	$Ru©5p_y$~1.4%	$Ru©5p_x$~9.3%	Ru©5px~9.1%	$Ru©5p_y$~12.1%	Ru©5px~12.3%
YRh						
	$Y©5p_x$~7.3%	$Y©5p_y$~8.1%	$Y©5p_x$~1.6%	$Y©5p_y$~2.0%	$Y©5p_y$~2.0%	Y©5px~1.6%
	$Rh©5p_x$~8.5%	$Rh©5p_y$~12.1%	$Rh©5p_x$~16.9%	$Rh©5p_y$~15.4%	$Rh©5p_y$~17.2%	Rh©5px~11.4%

Figure S6. Comparative analysis of 5p-orbital contributions to Metal-Center bonding in $NbTcM_4$ (M = Au/Ag/Cu), $ZrRuM_4$, and $YRhM_4$ systems at PBE0/Def2-TZVP Level.

Table S1. The lowest-lying isomer of $NbTcAu_4$ with energy in kcal·mol^{-1}. The distance between Nb-Tc is also given. These structures are re-optimized and filtrated at the PBE0/Def2-TZVP level.

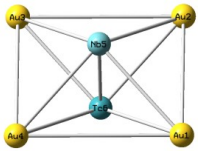
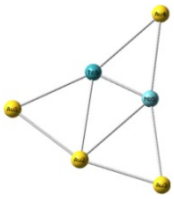
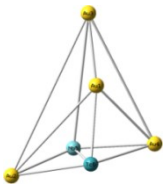
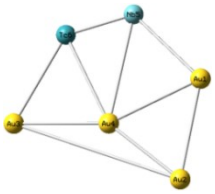
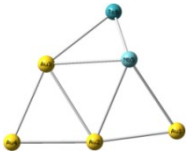
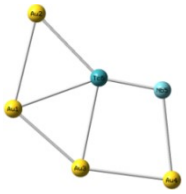
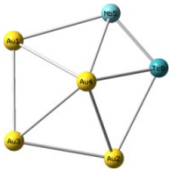
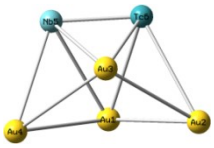
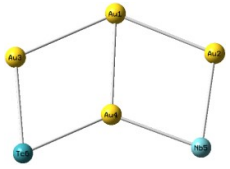
I  1.980 Å C_{4v}, ΔE=0.00	**II**  1.951 Å C_1, ΔE=1.7	**III**  1.968 Å C_1, ΔE=20.1
IV  1.920 Å C_s, ΔE=24.3	**V**  1.959 Å C_1, ΔE=25.3	**VI**  1.908 Å C_s, ΔE=25.8
VII  1.959 Å C_1, ΔE=36.5	**VIII**  2.046 Å C_s, ΔE=38.0	**IX**  4.580 Å C_s, ΔE=168.6

Table S2. Symmetry-breaking study of C_{4v}-$NbTcAu_4$ corresponding to conformer I at the PBE0/Def2-TZVP level.

Multiplicity	1	3	5	7	9
ΔE (kcal·mol^{-1})	0.0	15.4	49.3	86.3	151.4

Table S3. Energy differences (ΔE, kcal·mol^{-1}) for the conformer II (ΔE II-I) and triplet state (ΔE T-S) relative to the global minimum (conformer I, Singlet).

Method/Basis set	ΔE II-I (kcal·mol^{-1})	ΔE T-S (kcal·mol^{-1})
TPSSH/Def2-TZVP	3.3	4.0
PBE0/Def2-QZVP	99.3	2.2
M06-L/Def2-TZVP	1.9	6.0
HSE06/Def2-TZVP	0.2	1.2

Table S4. The energy of the structure $NbTcAu_4$ in different multiplicity at the PBE0/Def2-TZVP level.

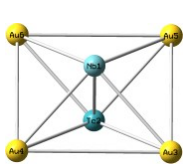
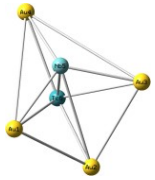
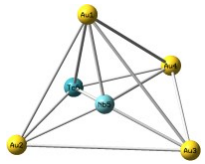
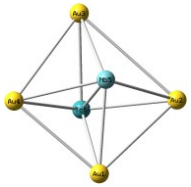
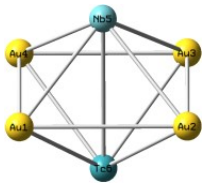
Multiplicity	1	3	5	7	9
Diagrams					
Distance (Å)	1.980	2.102	2.410	2.582	2.666
ΔE (kcal·mol^{-1})	0.0	1.2	16.8	26.9	34.5

Table S5. The Nb-Tc bond length, WBI and Mayer bond index results of C_{4v}-$NbTcAu_4$ calculated at different methods and basis set level.

Methond/Basis set	R_{Nb-Tc}(Å)	WBI	Mayer
B3LYP/Def2-TZVP	2.000	3.999	3.762
CCSD/Def2-TZVP	1.998	3.733	3.706
TPSSH/Def2-TZVP	2.013	3.979	3.807
PBE0/Def2-TZVP	1.980	4.054	3.875
PBE0/Def2-QZVP	1.967	4.100	4.176
CAM-B3LYP-D3/Def2-TZVP	1.971	4.001	3.793
B2PLYP-D3/Def2-TZVP	2.059	3.890	3.699
M06-L/Def2-TZVP	2.013	4.058	3.856
HSE06/Def2-TZVP	1.985	4.050	3.696

Table S6. The lowest-lying isomer of D_{4h}-Mo_2Au_4 with energy in kcal·mol^{-1}. The distance between Mo_2 is also given. These structures are re-optimized and filtrated at the PBE0/Def2-TZVP level.

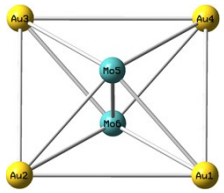
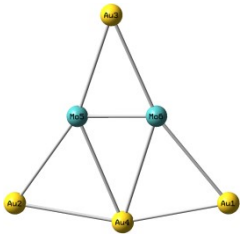
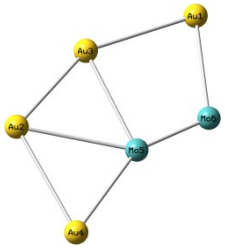
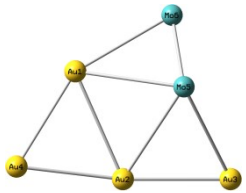
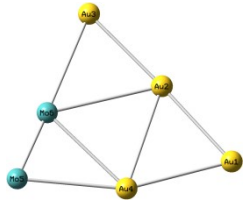
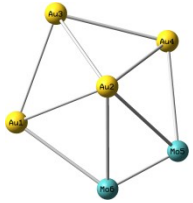
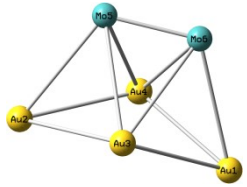
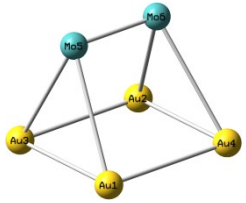
I	**II**	**III**	**IV**
			
1.947 Å	1.928 Å	1.890 Å	1.935 Å
D_{4h} , ΔE=0.00	C_1 , ΔE=3.73	C_1 , ΔE=20.87	C_1 , ΔE=24.62
V	**VI**	**VII**	**VIII**
			
1.926 Å	1.932 Å	1.982 Å	1.906 Å
C_1 , ΔE=26.17	C_s , ΔE=35.15	C_1 , ΔE=40.48	C_1 , ΔE=40.86

Table S7. The lowest-lying isomer of C_1-$ZrRuAu_4$ with energy in kcal·mol^{-1}. The distance between Zr-Ru is also given. These structures are re-optimized and filtrated at the PBE0/Def2-TZVP level.

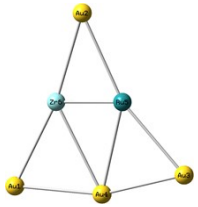
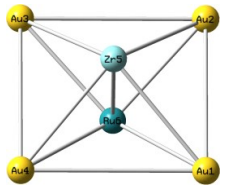
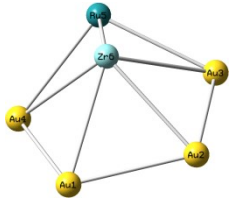
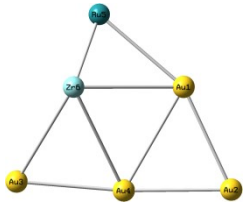
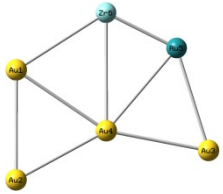
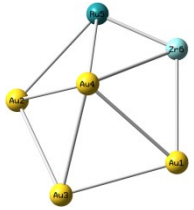
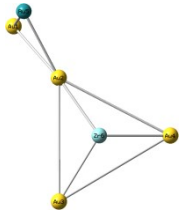
I	**II**	**III**	**IV**
			
2.030 Å	2.075 Å	2.110 Å	2.039 Å
C_1 , ΔE=0.00	C_{4v} , ΔE=0.20	C_1 , ΔE=16.73	C_1 , ΔE=21.12
V	**VI**	**VII**	
			
1.996 Å	2.046 Å	4.829 Å	
C_1 , ΔE=24.50	C_s , ΔE=35.17	C_1 , ΔE=120.03	

Table S8. The lowest-lying isomer of C_1-$YRhAu_4$ with energy in kcal·mol^{-1}. The distance between Y-Rh is also given. These structures are re-optimized and filtrated at the PBE0/Def2-TZVP level.

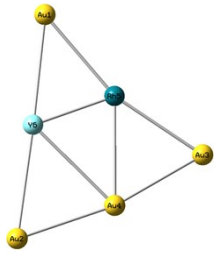
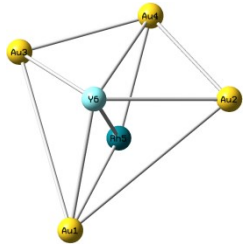
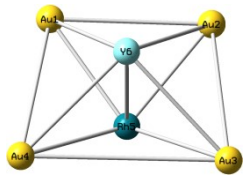
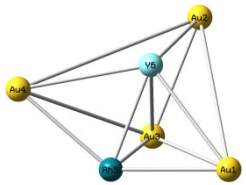
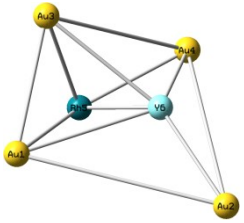
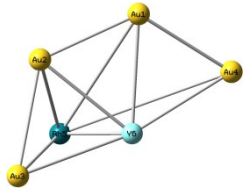
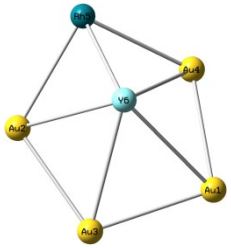
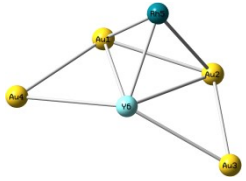
I	II	III	IV
			
2.225 Å	2.263 Å	2.289 Å	2.394 Å
C_1, ΔE=0.00	C_s, ΔE=3.08	C_1, ΔE=5.57	C_1, ΔE=7.72
V	**VI**	**VII**	**VIII**
			
2.392 Å	2.276 Å	2.356 Å	2.329 Å
C_1, ΔE=8.61	C_s, ΔE=10.83	C_1, ΔE=11.91	C_1, ΔE=14.11

Table S9. The lowest-lying isomer of C_1-$NbTcAg_4$ with energy in kcal·mol^{-1}. The distance between Nb-Tc is also given. These structures are re-optimized and filtrated at the PBE0/Def2-TZVP level.

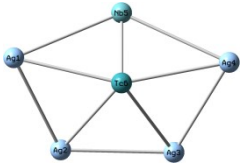
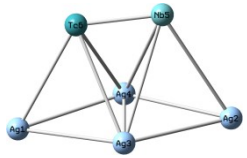
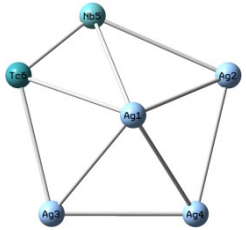
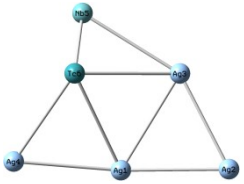
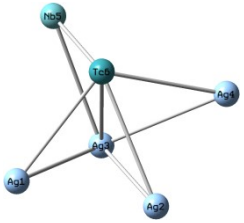
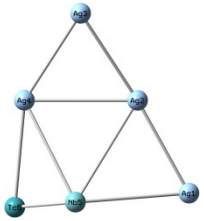
I	**II**	**III**	**IV**
			
1.940 Å C_1 , ΔE=0.00	1.956 Å C_1 , ΔE=4.13	1.962 Å C_1 , ΔE=13.82	1.938 Å C_1 , ΔE=14.75
V	**VI**	**VII**	
			
1.942 Å C_s , ΔE=17.70	1.963 Å C_s , ΔE=17.91	1.944 Å C_1 , ΔE=19.69	

Table S10. The lowest-lying isomer of C_1-$ZrRuAg_4$ with energy in kcal·mol^{-1}. The distance between Zr-Ru is also given. These structures are re-optimized and filtrated at the PBE0/Def2-TZVP level.

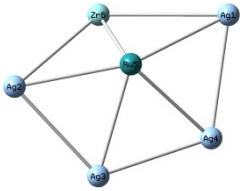
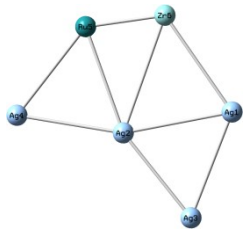
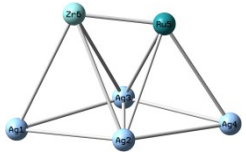
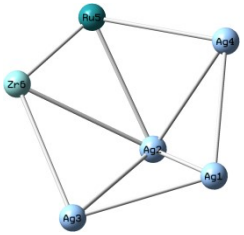
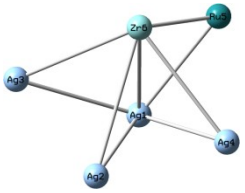
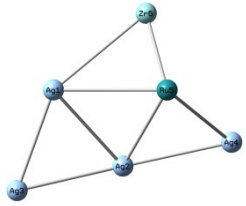
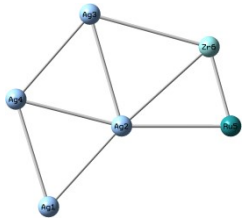
I	**II**	**III**	**IV**
			
2.015 Å C_1, ΔE=0.00	2.035 Å C_1, ΔE=0.48	1.997 Å C_1, ΔE=12.48	2.049 Å C_1, ΔE=13.11
V	**VI**	**VII**	**VIII**
			
2.017 Å C_1, ΔE=13.62	2.064 Å C_s, ΔE=14.66	2.016 Å C_1, ΔE=15.91	2.014 Å C_1, ΔE=19.84

Table S11. The lowest-lying isomer of C_1-$YRhAg_4$ with energy in kcal·mol^{-1}. The distance between Y-Rh is also given. These structures are re-optimized and filtrated at the PBE0/Def2-TZVP level.

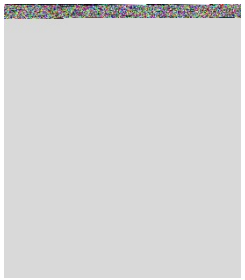
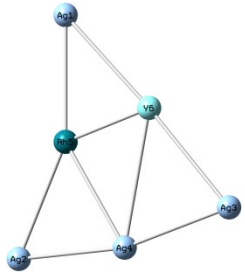
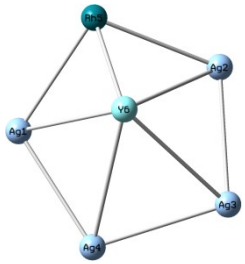
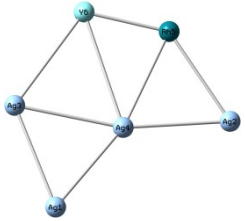
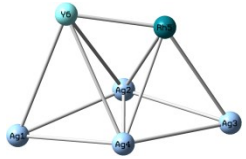
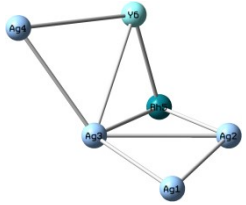
I	II	III
		
2.219 Å C_1 , ΔE=0.00	2.194 Å C_1 , ΔE=2.63	2.255 Å C_1 , ΔE=10.29
IV	**V**	**VI**
		
2.171 Å C_1 , ΔE=14.46	2.247 Å C_1 , ΔE=16.10	2.208 Å C_1 , ΔE=16.69

Table S12. The lowest-lying isomer of C_1-$NbTcCu_4$ with energy in kcal·mol^{-1}. The distance between Nb-Tc is also given. These structures are re-optimized and filtrated at the PBE0/Def2-TZVP level.

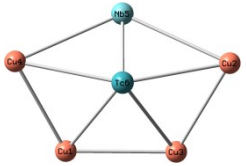
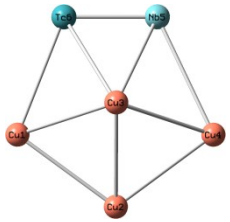
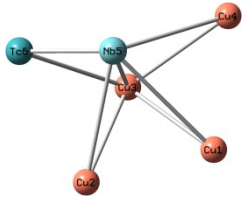
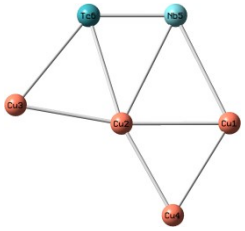
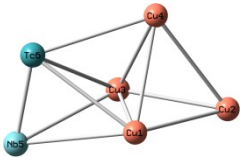
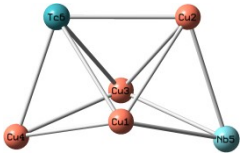
I	**II**	**III**	**IV**
			
1.976 Å C_1 , ΔE=0.00	1.976Å C_1 , ΔE=0.13	1.948Å C_1 , ΔE=5.22	1.999 Å C_1 , ΔE=5.35
V	**VI**	**VII**	
			
1.936 Å C_1 , ΔE=7.84	1.985 Å C_s , ΔE=8.34	4.076 Å C_1 , ΔE=129.60	

Table S13. The lowest-lying isomer of C_1-$ZrRuCu_4$ with energy in kcal·mol^{-1}. The distance between Zr-Ru is also given. These structures are re-optimized and filtrated at the PBE0/Def2-TZVP level.

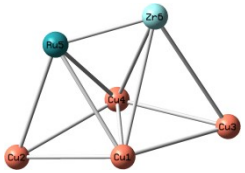
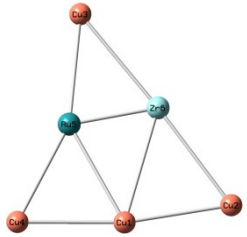
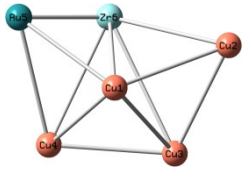
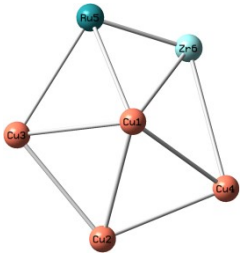
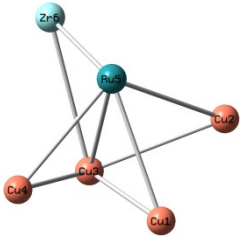
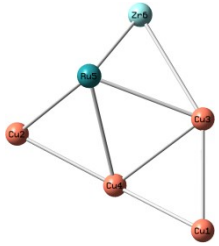
I	II	III	IV
			
2.059 Å C_1 , ΔE=0.00	2.062 Å C_1 , ΔE=3.95	2.029 Å C_1 , ΔE=3.96	2.080 Å C_1 , ΔE=7.56
V	**VI**	**VII**	
			
2.029 Å C_1 , ΔE=8.54	2.056 Å C_1 , ΔE=8.79	2.033 Å C_1 , ΔE=15.09	

Table S14. The lowest-lying isomer of C_1-$YRhCu_4$ with energy in kcal·mol^{-1}. The distance between Y-Rh is also given. These structures are re-optimized and filtrated at the PBE0/Def2-TZVP level.

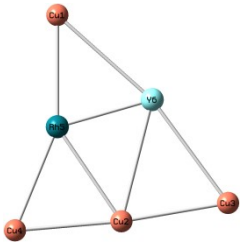
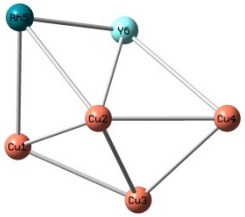
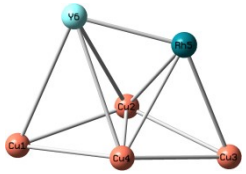
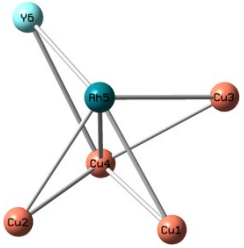
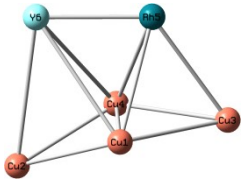
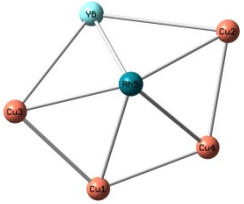
I	**II**	**III**	**IV**
			
2.250 Å C_1 , ΔE=0.00	2.211 Å C_1 , ΔE=7.03	2.269 Å C_1 , ΔE=7.57	2.265 Å C_1 , ΔE=7.67
V	**VI**	**VII**	
			
2.252 Å C_1 , ΔE=7.75	2.265 Å C_s , ΔE=16.27	2.249 Å C_1 , ΔE=17.91	

Table S15. The energy of the structure D_{4h}-Mo_2Au_4 in different multiplicity at the PBE0/Def2-TZVP level.

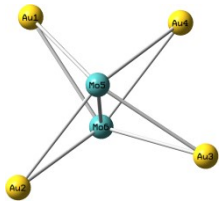
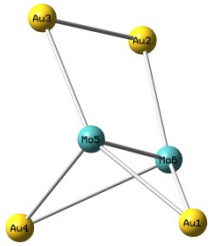
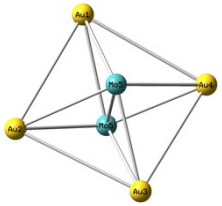
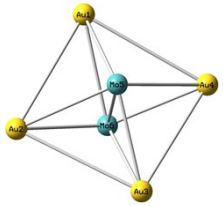
Multiplicity	1	3	5	7	9
Diagrams					
Distance (Å)	1.947	2.023	2.078	2.339	2.719
ΔE (kcal·mol^{-1})	0.0	3.9	21.8	42.7	37.4

Table S16. The energy of the structure $ZrRuAu_4$ in different multiplicity at the PBE0/Def2-TZVP level.

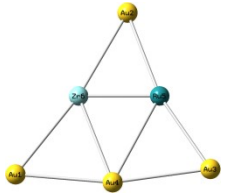
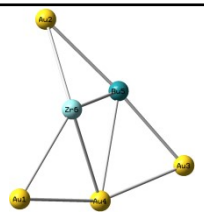
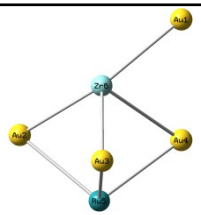
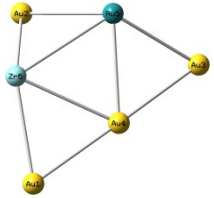
Multiplicity	1	3	5	7	9
Diagrams					
Distance (Å)	2.030	2.182	2.370	2.852	2.958
ΔE (kcal·mol^{-1})	0.0	17.1	36.5	36.0	86.6

Table S17. The energy of the structure $YRhAu_4$ in different multiplicity at the PBE0/Def2-TZVP level.

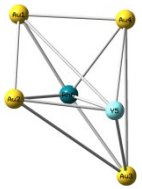
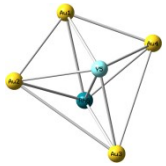
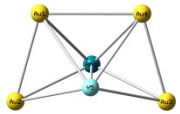
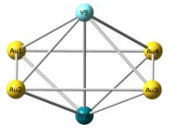
Multiplicity	1	3	5	7	9
Diagrams					
Distance (Å)	2.225	2.479	2.799	3.019	3.181
ΔE (kcal·mol^{-1})	0.0	8.0	25.0	68.7	134.8

Table S18. The energy of the structure $NbTcAg_4$ in different multiplicity at the PBE0/Def2-TZVP level.

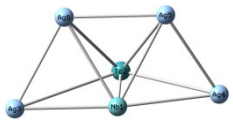
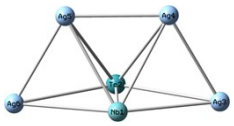
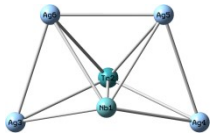
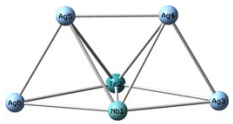
Multiplicity	1	3	5	7	9
Diagrams					
Distance (Å)	1.940	2.084	2.128	2.517	2.689
ΔE (kcal·mol^{-1})	0.0	8.5	21.1	39.7	39.8

Table S19. The energy of the structure $ZrRuAg_4$ in different multiplicity at the PBE0/Def2-TZVP level.

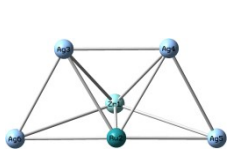
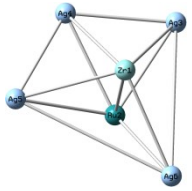
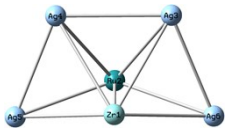
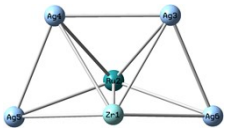
Multiplicity	1	3	5	7	9
Diagrams					
Distance (Å)	2.015	2.076	2.295	2.455	2.811
ΔE (kcal·mol^{-1})	0.0	10.7	31.2	45.1	75.9

Table S20. The energy of the structure $YRhAg_4$ in different multiplicity at the PBE0/Def2-TZVP level.

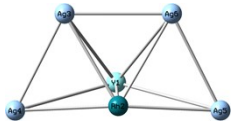
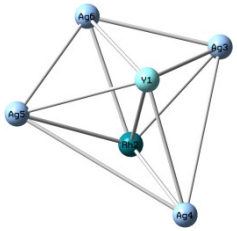
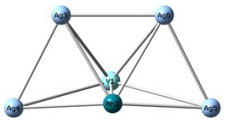
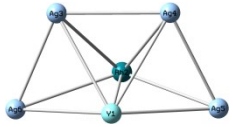
Multiplicity	1	3	5	7	9
Diagrams					
Distance (Å)	2.219	2.293	2.684	2.820	2.797
ΔE (kcal·mol^{-1})	0.0	10.4	34.0	69.0	143.4

Table S21. The energy of the structure $NbTcCu_4$ in different multiplicity at the PBE0/Def2-TZVP level.

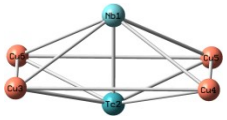
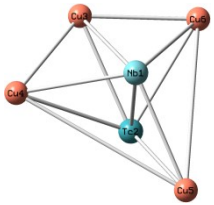
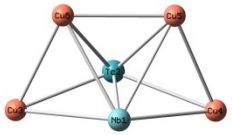
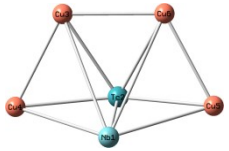
Multiplicity	1	3	5	7	9
Diagrams					
Distance (Å)	1.976	2.035	2.176	2.443	2.898
ΔE (kcal·mol^{-1})	0.0	10.1	18.5	25.2	38.4

Table S22. The energy of the structure $ZrRuCu_4$ in different multiplicity at the PBE0/Def2-TZVP level.

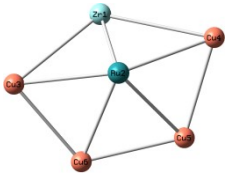
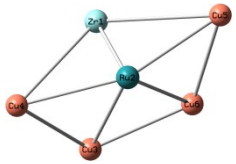
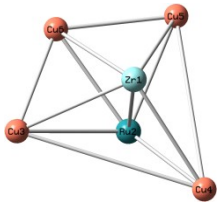
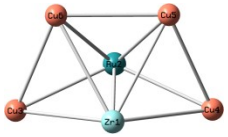
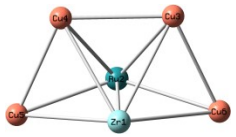
Multiplicity	1	3	5	7	9
Diagrams					
Distance (Å)	2.059	2.099	2.323	2.660	2.775
ΔE (kcal·mol^{-1})	0.0	6.0	24.5	35.7	67.0

Table S23. The energy of the structure $YRhCu_4$ in different multiplicity at the PBE0/Def2-TZVP level.

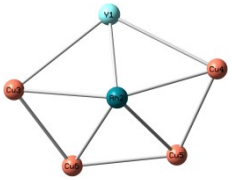
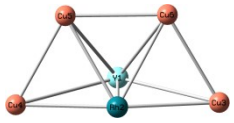
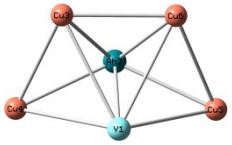
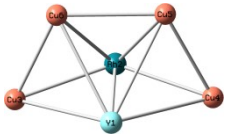
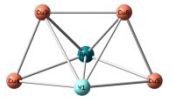
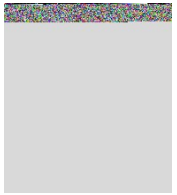
Multiplicity	1	3	5	7	9
Diagrams					
Distance (Å)	2.250	2.323	2.706	2.810	3.098
ΔE (kcal·mol^{-1})	0.0	6.7	28.0	63.1	122.0

Table S24. The orbital component analysis results of C_{4v}-$NbTcAu_4$ calculated at the PBE0/Def2-TZVP level.

C_{4v}-$NbTcAu_4$	HOMO	HOMO-1		HOMO-2
Diagrams				
Energy/eV	-6.00	-6.17		-6.75
Component	Au_4©$5d_{x^2-y^2}$ ~ 21.9% Nb©$4d_{xy}$ ~ 10.3% Tc©$4d_{x^2-y^2}$ ~ 65.1%	Au_4©6s ~ 54.5% Nb©$5p_x$ ~ 11.3% Nb©$4d_{xz}$ ~ 3.3% Tc©$5p_x$ ~ 10.0% Tc©$4d_{xz}$ ~ 10.7%	Au_4©6s ~ 54.9% Nb©$5p_y$ ~ 11.3% Nb©$4d_{yz}$ ~ 3.2% Tc©$5p_y$ ~ 10.0% Tc©$4d_{yz}$ ~ 10.7%	Au_4©6s ~ 25.1% Au_4©$5d_{xy}$ ~ 36.7% Nb©$4d_{x^2-y^2}$ ~ 15.3% Tc©$4d_{x^2-y^2}$ ~ 19.8%

C_{4v}-$NbTcAu_4$	HOMO-3		HOMO-4	HOMO-19
Diagrams				
Energy/eV	-7.47		-7.63	-10.43
Component	Au_4©$5d_{xy}$ ~ 12.3% Au_4©$5d_{x^2-y^2}$ ~ 32.1% Au_4©$5d_{z^2}$ ~ 10.7% Nb©$4d_{xz}$ ~ 11.7% Tc©$4d_{xz}$ ~ 22.8%	Au_4©$5d_{xy}$ ~ 12.3% Au_4©$5d_{x^2-y^2}$ ~ 32.1% Au_4©$5d_{z^2}$ ~ 10.7% Nb©$4d_{yz}$ ~ 11.7% Tc©$4d_{yz}$ ~ 22.8%	Au_4©6s ~ 15.3% Nb©5s ~ 9.5% Nb©$4d_{z^2}$ ~ 22.8% Tc©5s ~ 6.1% Tc©$4d_{z^2}$ ~ 32.8%	Au_4©6s ~ 14.9% Au_4©$5d_{x^2-y^2}$ ~ 30.4% Au_4©$5d_{z^2}$ ~ 9.6% Nb©5s ~ 9.0% Nb©$4d_{z^2}$ ~ 5.8% Nb©$5p_z$ ~ 3.2% Tc©5s ~ 7.4% Tc©$4d_{z^2}$ ~ 8.8% Tc©$5p_z$ ~ 3.0%

The coefficient of each orbital is given by the contribution of the Au_4, Nb and Tc fragments.

Table S25. The orbital component analysis results of D_{6h}-Nb_2Au_6 calculated at the PBE0/Def2-TZVP level.

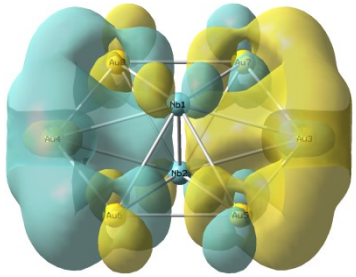
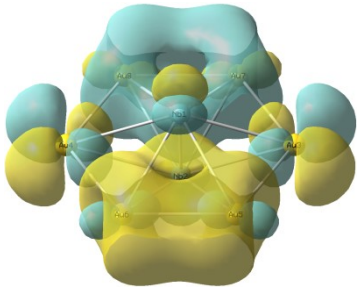
D_{6h}-Nb_2Au_6	HOMO-3	
Diagrams		
Energy/eV	-7.40	
Component	Nb_2©4dxz ~ 9.9%	Nb_2©$4d_{xz}$ ~ 9.9%
	Nb_2©$5p_{x, y}$ ~ 7.5%	Nb_2©$5p_{x, y}$ ~ 7.5%
	Au_6©6s ~ 23.5%	Au_6©6s ~ 21.5%
	Au_6©$5d_{xy}$ ~ 44.6%	Au_6©$5d_{x^2-y^2}$ ~ 43.8%

Table S26. Vertical electron affinity of the D_{6h}-Nb_2Au_6 and C_{4v}-$NbTcAu_4$ clusters at the PBE0/Def2-TZVP level.

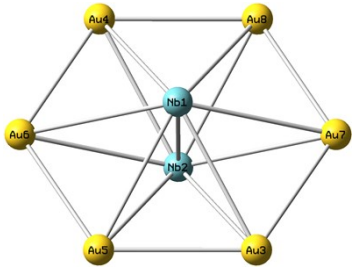
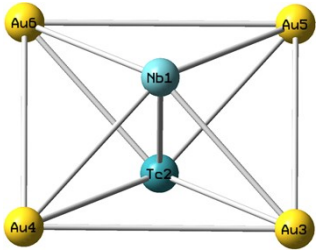
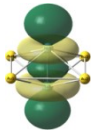
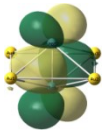
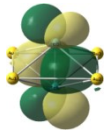
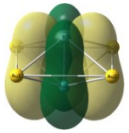
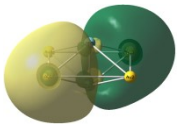
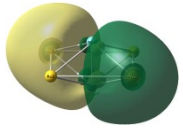
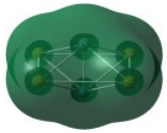
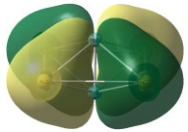
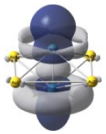
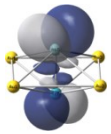
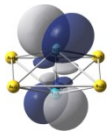
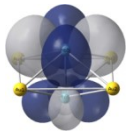
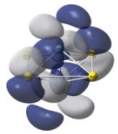
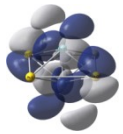
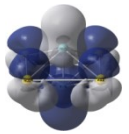
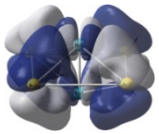
Cluster	D_{6h}-Nb_2Au_6	D_{6h}-$Nb_2Au_6^-$	C_{4v}-$NbTcAu_4$	C_{4v}-$NbTcAu_4^-$
Structure				
Electronic Energy /a.u.	-928.5774233	-928.6414583	-680.8218021	-680.8821058
VEA /(kcal·mol^{-1})	40.2		37.8	

Table S27. (a) Bonding / Antibonding molecular orbitals governing Nb-Tc bonding with occupation numbers (isovalue = 0.02).

							
2c-2e σ bond ON=2.00 |e|	2×2c-2e π bond ON=2.00 |e|		2c-2e δ bond ON=1.97 |e|	2×4c-2e π bond ON=1.98 |e|		6c-2e σ bond ON=2.00 |e|	6c-2e δ bond ON=2.00 |e|
							
2c-2e σ* bond ON=0.03 |e|	2×2c-2e π* bond ON=0.17 |e|		2c-2e δ* bond ON=0.10 |e|	2×4c-2e π* bond ON=0.04 |e|		6c-2e σ* bond ON=0.01 |e|	6c-2e δ* bond ON=0.01 |e|

(b): Effective bond order calculation parameters (η_a: antibonding orbital occupation; η_b: bonding orbital occupation).

$$\mathrm{EBO}_{NbTc} = \eta_b - \eta_a / 2 = 7.43$$

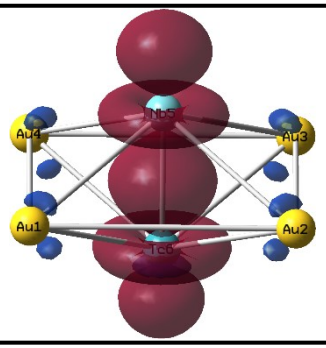
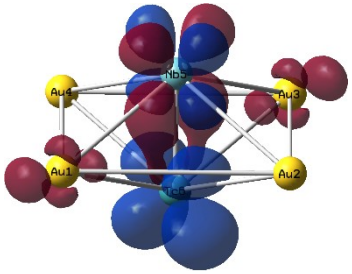
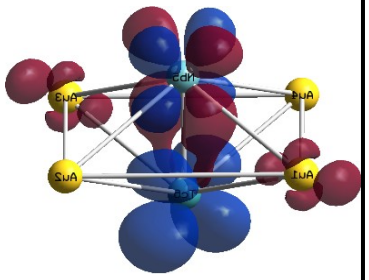
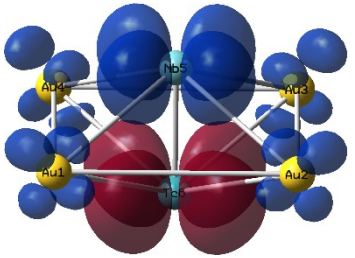
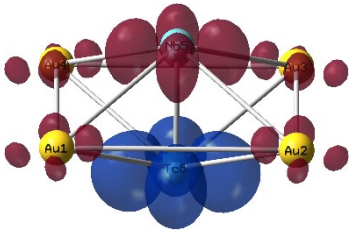
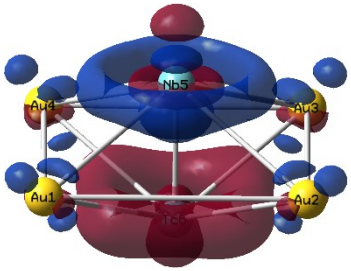
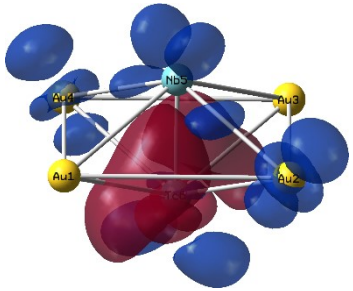
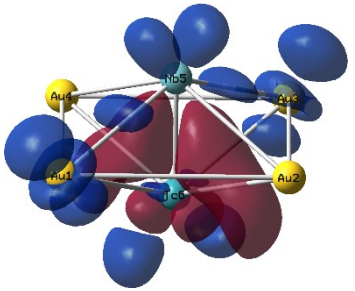
Table S28. The bond length $R_{M-M'}$, ω_e, AIP-AEA, ρ(BCP), $\nabla^2\rho$, H(r) and EBO data of C_{4v}-$NbTcAu_4$, RhSc, Mo_2 and W_2 dimers.

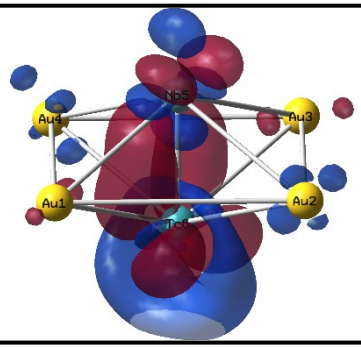
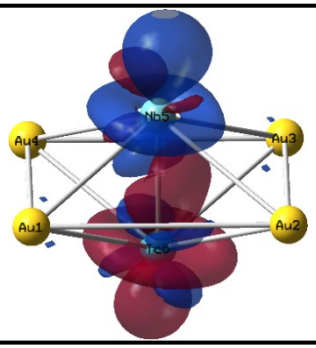
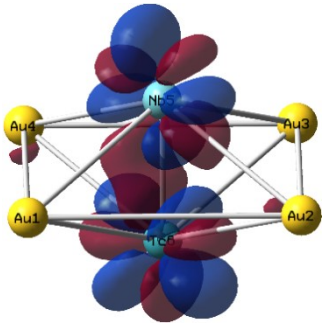
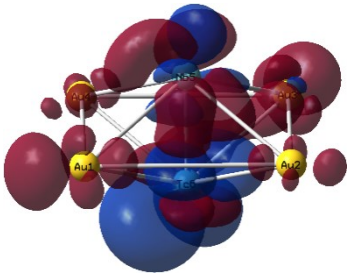
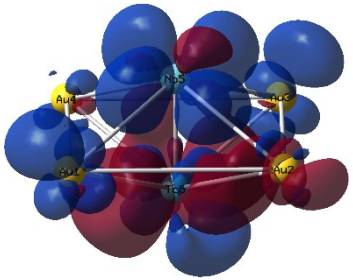
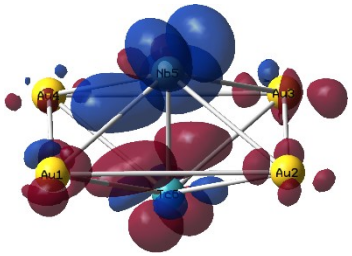
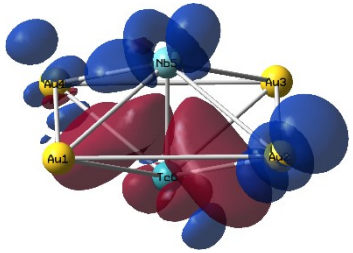
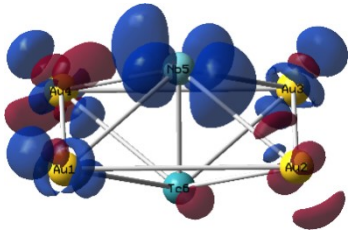
Property/Systems	C_{4v}-$NbTcAu_4$	RhSc	Mo_2	W_2
$R_{M-M'}$[Å]	1.980	1.961	1.887	1.991
ω_e [cm^{-1}]	512.43	498.65	597.99	420.64
AIP [eV]	6.90	6.48	6.73	6.54
AEA [eV]	2.05	0.53	0.69	1.05
ρ	0.248	0.186	0.298	0.255
$\nabla^2\rho$	0.674	0.778	0.898	0.783
H(r)	-0.192	-0.972	-0.262	-0.194
EBO	7.43	5.7	5.2	5.2

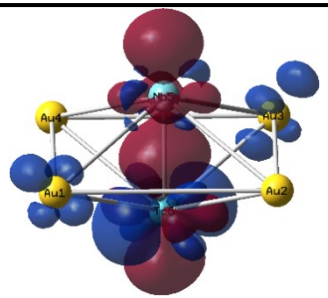
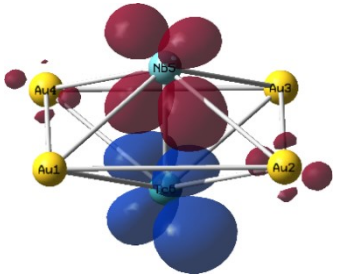
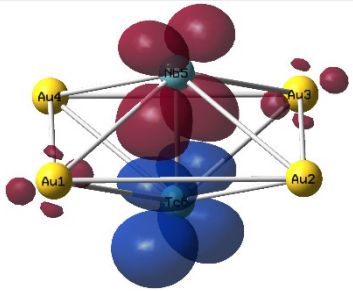
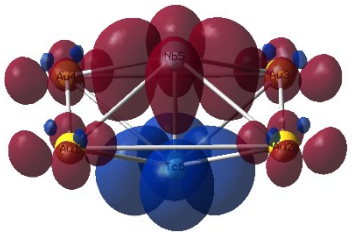
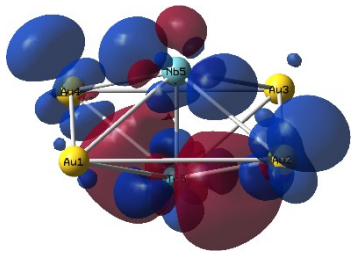
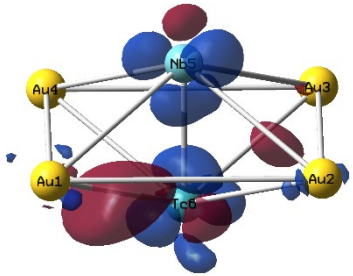
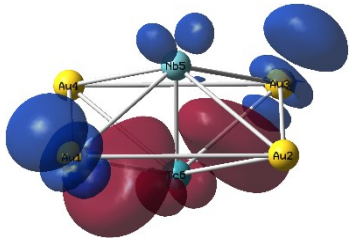
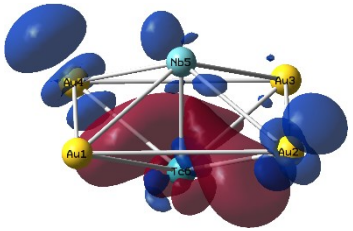
Table S29. Plot of the EDA-NOCV pair of the main intrinsic interaction energy(ΔE_{int}) at the PBE0/Def2-TZVP level.

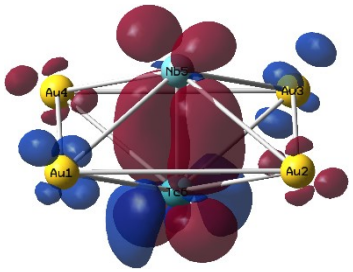
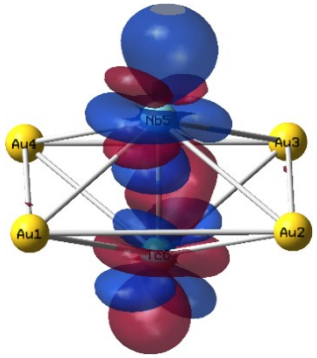
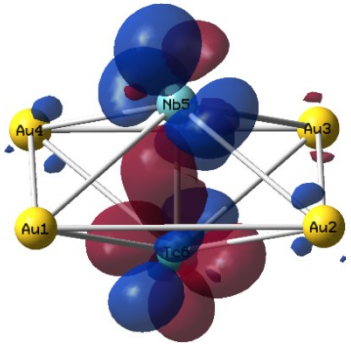
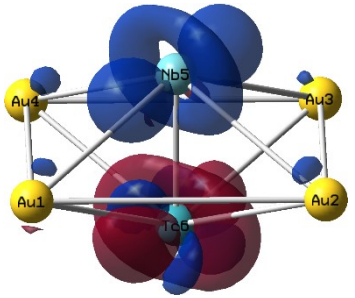
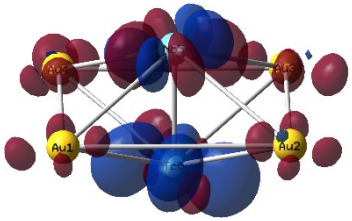
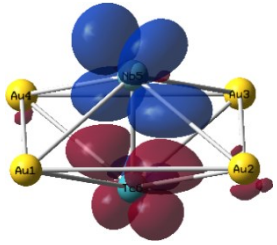
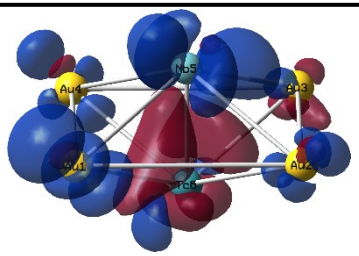
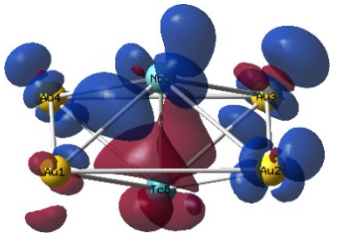
Scheme	Fragmentation	Multiplicity	ΔE_{int} /(kcal·mol^{-1})	Charge Flow Direction
A	$^{1}[NbAu_4]^{+} + {}^{1}[Tc]^{-}$	Singlet	-2081.18	
B	$^{2}[NbAu_4] + {}^{2}[Tc]$	Doublet	-1147.25	
C	$^{3}[NbAu_4]^{+} + {}^{3}[Tc]^{-}$	Triplet	-1865.33	
D	$^{4}[NbAu_4] + {}^{4}[Tc]$	Quartet	-1109.51	
E	$^{5}[NbAu_4]^{+} + {}^{5}[Tc]^{-}$	Quintet	-1868.91	blue → red
F	$^{6}[NbAu_4] + {}^{6}[Tc]$	Sextet	-1176.32	
G	$^{7}[NbAu_4]^{+} + {}^{7}[Tc]^{-}$	Septet	-2181.07	
H	$^{8}[NbAu_4] + {}^{8}[Tc]$	Octet	-1512.11	
I	$^{9}[NbAu_4]^{+} + {}^{9}[Tc]^{-}$	Nonet	-2299.32	

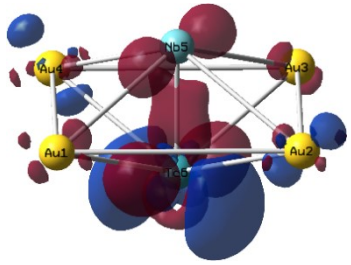
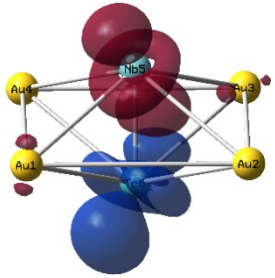
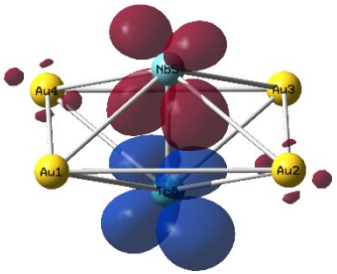
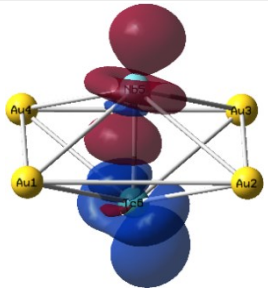
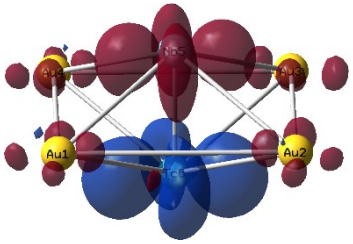
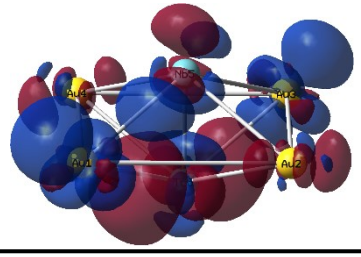
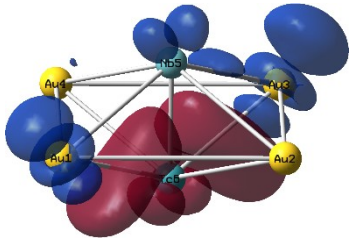
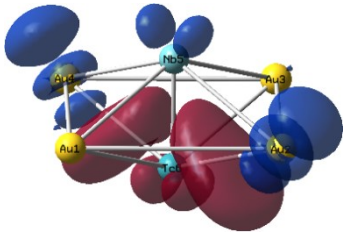
The energy order is consistent with the orbital interactions shown in Figure 1 of the main text.

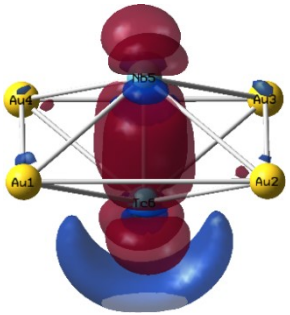
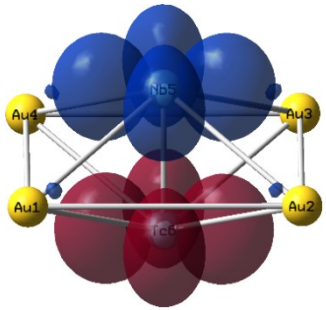
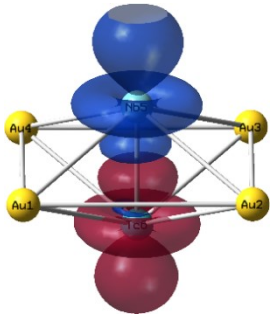
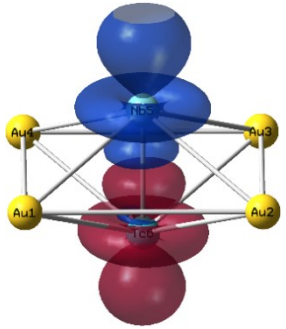
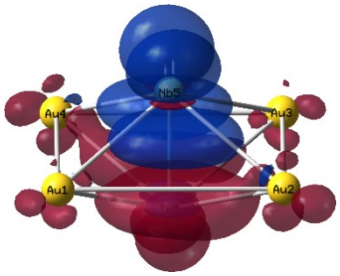
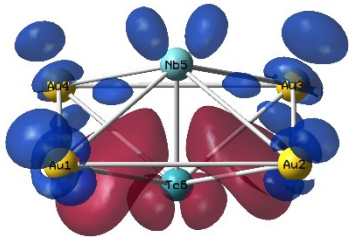
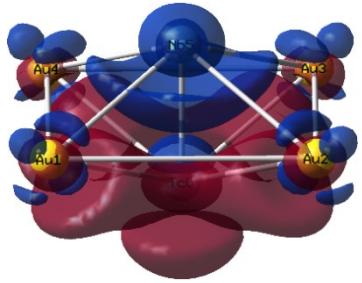
Scheme A. $[NbAu_4]^+$ fragment and $[Tc]^-$ fragment NOCV orbitals				
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}1}$ = -575.76	$\Delta E_{orb\text{-}2}$ = -140.98	$\Delta E_{orb\text{-}3}$ = -140.98	$\Delta E_{orb\text{-}4}$ = -92.02
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}5}$ = -29.43	$\Delta E_{orb\text{-}6}$ = -26.76	$\Delta E_{orb\text{-}7}$ = -8.53	$\Delta E_{orb\text{-}8}$ = -8.53
ΔE = -1022.99 kcal·mol^{-1}				

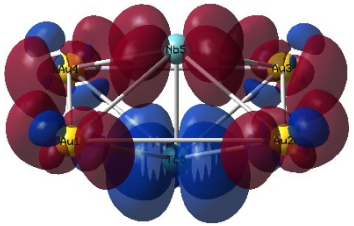
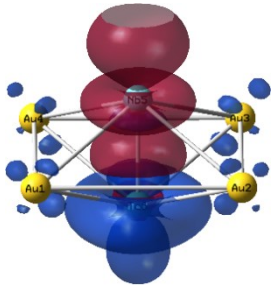
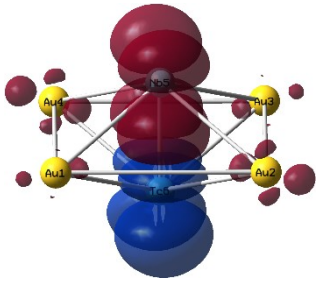
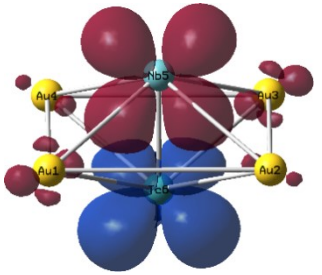
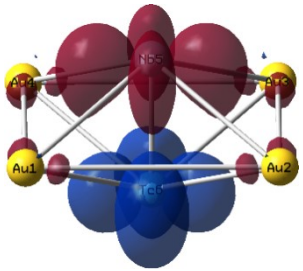
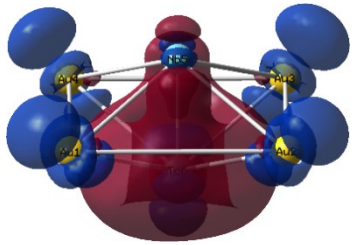
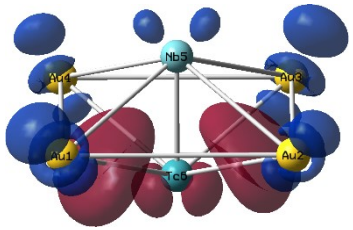
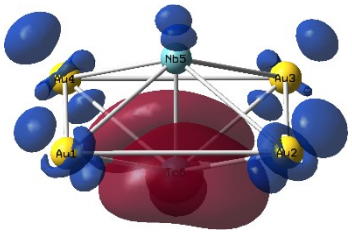
Scheme B. $^{2}[NbAu_4]$ **fragment and** $^{2}[Tc]$ **fragment α NOCV orbitals**				
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}1\alpha}$ = -243.43	$\Delta E_{orb\text{-}2\alpha}$ = -102.46	$\Delta E_{orb\text{-}3\alpha}$ = -70.84	$\Delta E_{orb\text{-}4\alpha}$ = -38.41
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}5\alpha}$ = -44.29	$\Delta E_{orb\text{-}6\alpha}$ = -6.99	$\Delta E_{orb\text{-}7\alpha}$ = -3.91	$\Delta E_{orb\text{-}8\alpha}$ = -4.34

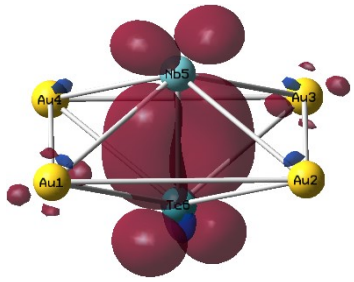
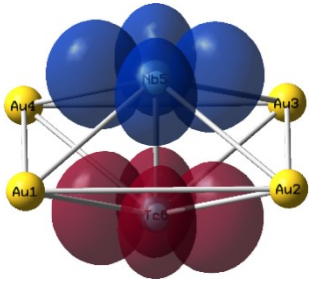
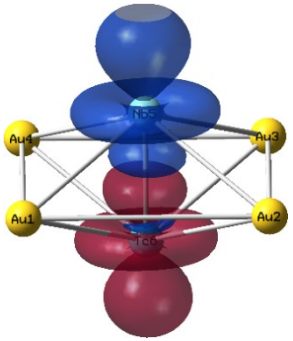
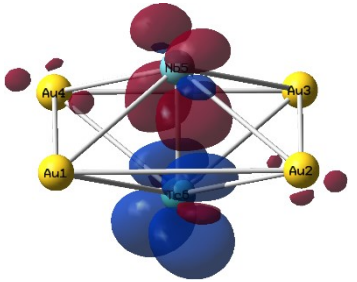
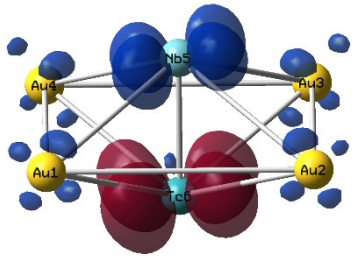
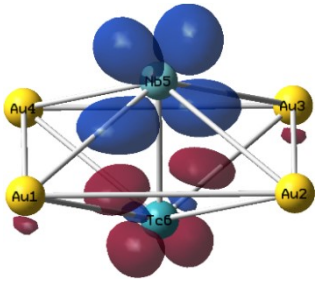
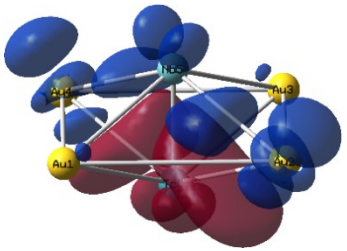
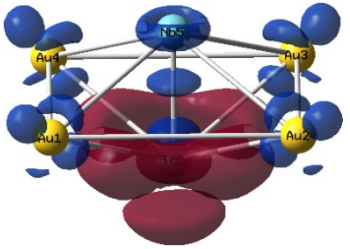
Scheme B. ^{2}[NbAu$_4$] fragment and ^{2}[Tc] fragment β NOCV orbitals				
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}1\beta}$ = -127.01	$\Delta E_{orb\text{-}2\beta}$ = -59.61	$\Delta E_{orb\text{-}3\beta}$ = -57.00	$\Delta_{orb\text{-}4\beta}$ = -15.43
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}5\alpha}$ = -20.50	$\Delta E_{orb\text{-}6\alpha}$ = -7.85	$\Delta E_{orb\text{-}7\alpha}$ = -3.23	$\Delta E_{orb\text{-}8\alpha}$ = -3.90
$\Delta E(\alpha+\beta)$ = -809.20 kcal·mol^{-1}				

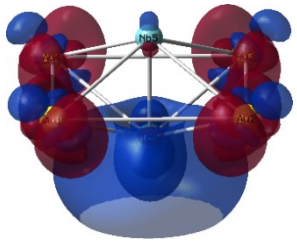
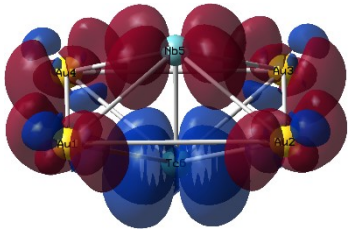
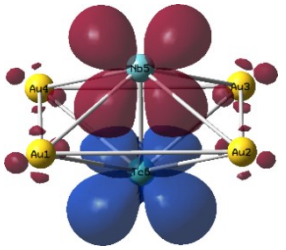
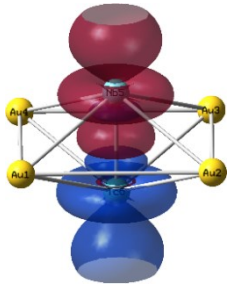
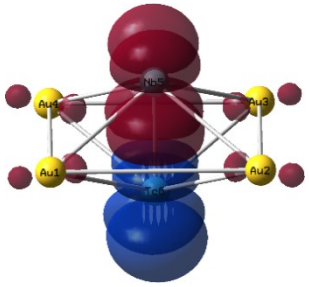
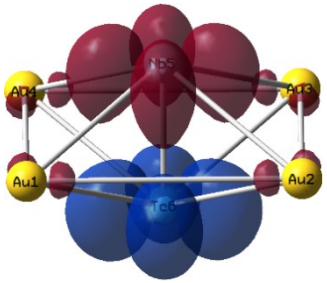
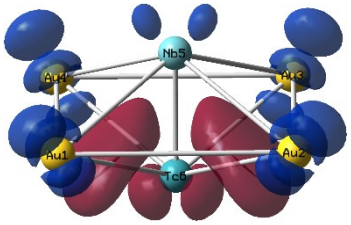
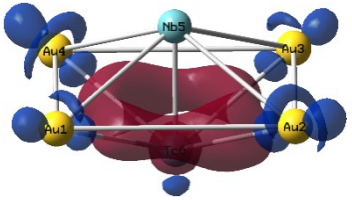
Scheme C. $^{3}[NbAu_4]^{+}$ **fragment and** $^{3}[Tc]^{-}$ **fragment α NOCV orbitals**				
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}1\alpha}$ = -260.08	$\Delta E_{orb\text{-}2\alpha}$ = -114.80	$\Delta E_{orb\text{-}3\alpha}$ = -75.36	$\Delta E_{orb\text{-}4\alpha}$ = -58.53
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}5\alpha}$ = -16.94	$\Delta E_{orb\text{-}6\alpha}$ = -20.40	$\Delta E_{orb\text{-}7\alpha}$ = -4.34	$\Delta E_{orb\text{-}8\alpha}$ = -5.64

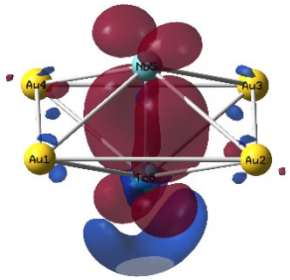
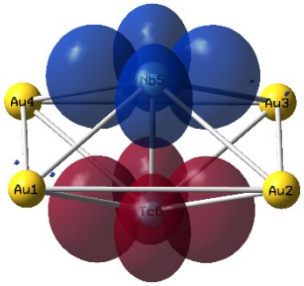
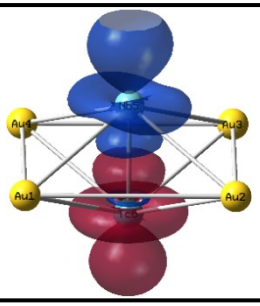
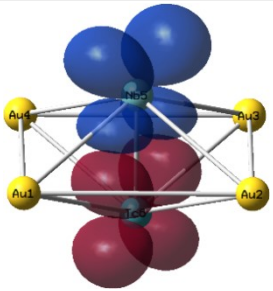
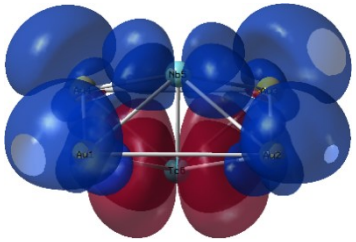
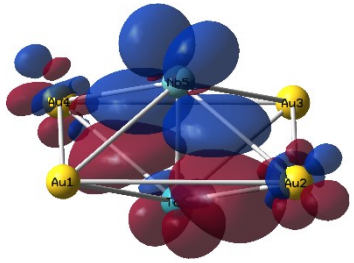
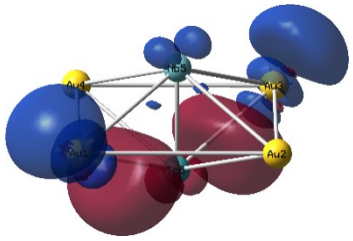
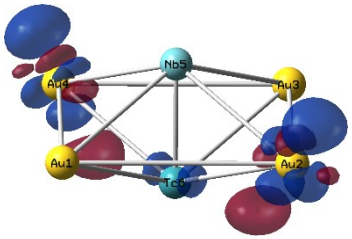
Scheme C. $^{3}[NbAu_4]^{+}$ fragment and $^{3}[Tc]^{-}$ fragment β NOCV orbitals				
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}1\beta}$ = -214.61	$\Delta E_{orb\text{-}2\beta}$ = -70.03	$\Delta E_{orb\text{-}3\beta}$ = -57.37	$\Delta E_{orb\text{-}4\beta}$ = -84.61
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}5\beta}$ = -16.50	$\Delta E_{orb\text{-}6\beta}$ = -10.44	$\Delta E_{orb\text{-}7\beta}$ = -3.87	$\Delta E_{orb\text{-}8\beta}$ = -3.64
$\Delta E(\alpha+\beta)$ = -1017.16 kcal·mol^{-1}				

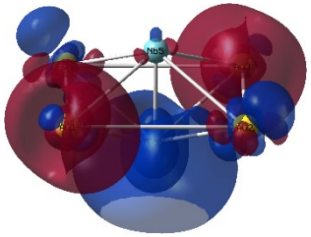
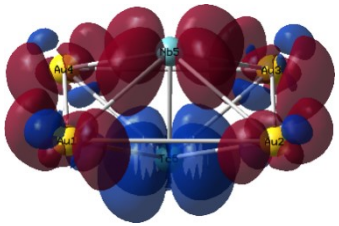
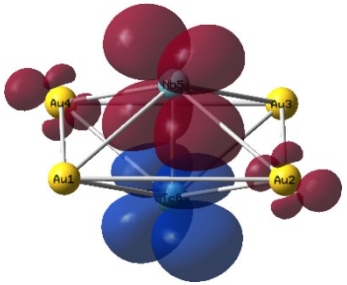
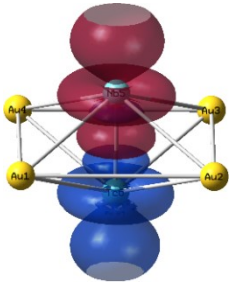
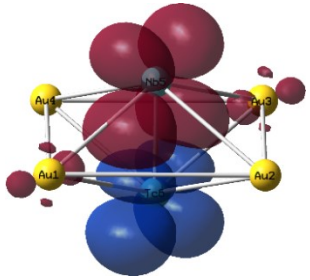
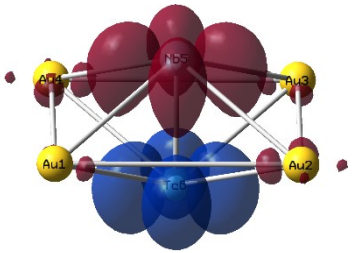
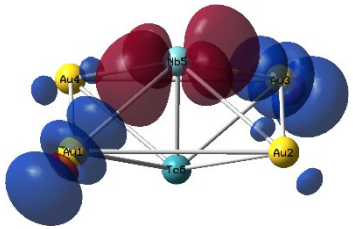
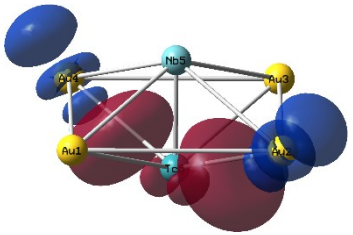
Scheme D. $^{4}[NbAu_4]$ **fragment and** $^{4}[Tc]$ **fragment α NOCV orbitals**				
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}1\alpha}$ = -266.42	$\Delta E_{orb\text{-}2\alpha}$ = -80.70	$\Delta E_{orb\text{-}3\alpha}$ = -112.25	$\Delta E_{orb\text{-}4\alpha}$ = -58.46
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}5\alpha}$ = -41.60	$\Delta E_{orb\text{-}6\alpha}$ = -10.19	$\Delta E_{orb\text{-}7\alpha}$ = -4.01	$\Delta E_{orb\text{-}8\alpha}$ = -14.90

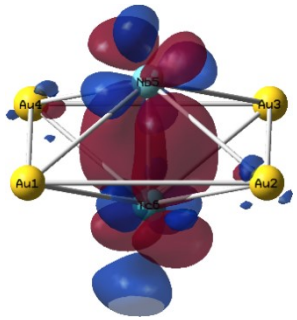
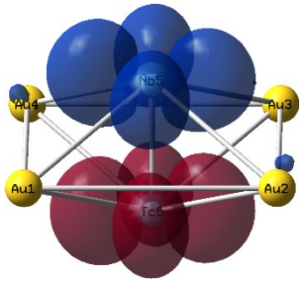
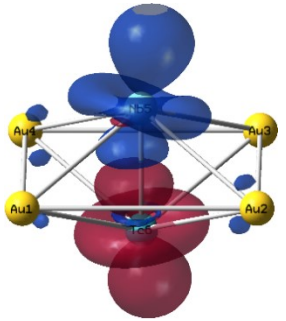
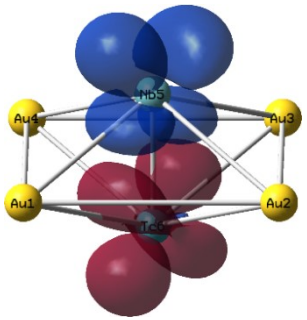
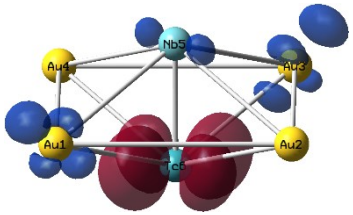
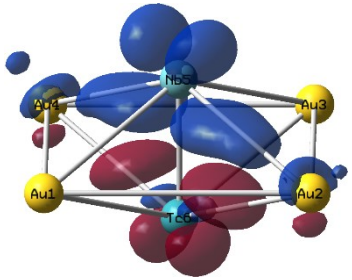
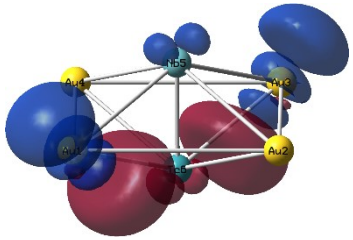
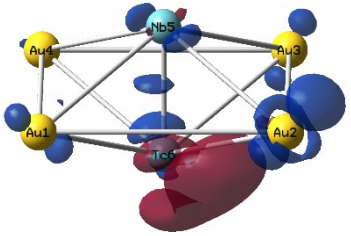
Scheme D. $^{4}[NbAu_4]$ **fragment and** $^{4}[Tc]$ **fragment β NOCV orbitals**				
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}1\beta}$ = -66.51	$\Delta E_{orb\text{-}2\beta}$ = -82.79	$\Delta E_{orb\text{-}3\beta}$ = -55.84	$\Delta_{orb\text{-}4\beta}$ = -55.22
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}5\alpha}$ = -19.04	$\Delta E_{orb\text{-}6\alpha}$ = -15.83	$\Delta E_{orb\text{-}7\alpha}$ = -2.92	$\Delta E_{orb\text{-}8\alpha}$ = -2.81
$\Delta E(\alpha+\beta)$ = -899.49 kcal·mol^{-1}				

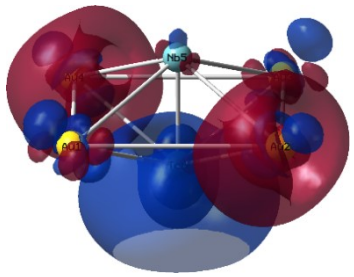
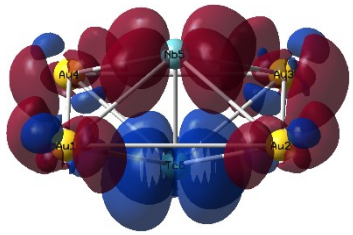
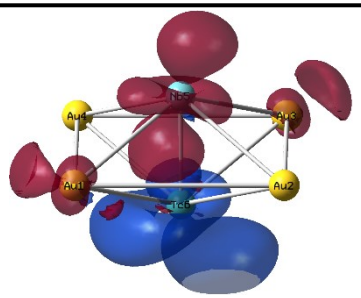
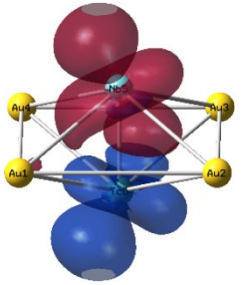
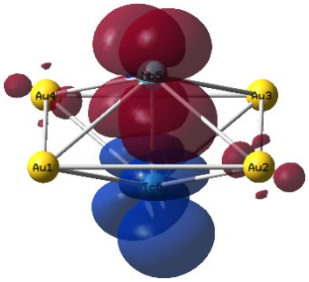
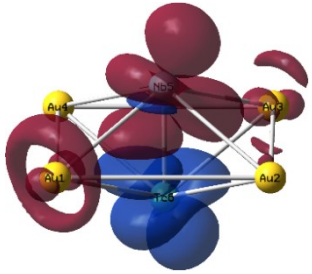
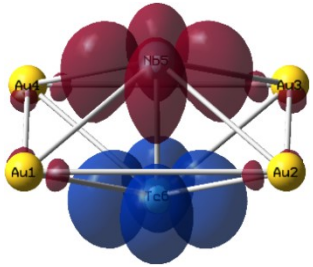
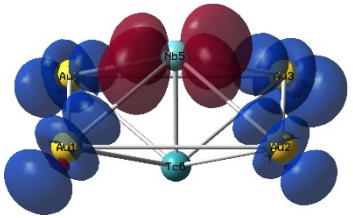
Scheme E. $^{5}[NbAu_4]^{+}$ fragment and $^{5}[Tc]^{-}$ fragment α NOCV orbitals				
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}1\alpha}$ = -322.63	$\Delta E_{orb\text{-}2\alpha}$ = -73.83	$\Delta E_{orb\text{-}3\alpha}$ = -118.28	$\Delta E_{orb\text{-}4\alpha}$ = -58.68
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}5\alpha}$ = -41.90	$\Delta E_{orb\text{-}6\alpha}$ = -11.41	$\Delta E_{orb\text{-}7\alpha}$ = -4.74	$\Delta E_{orb\text{-}8\alpha}$ = -17.85

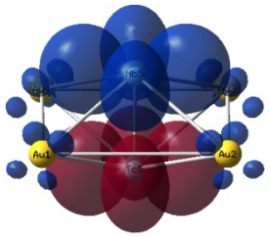
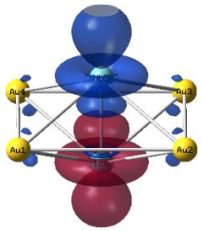
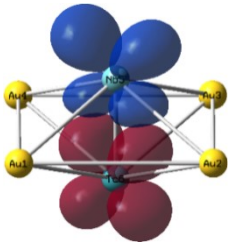
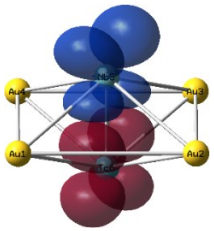
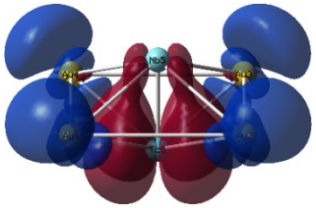
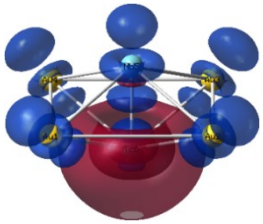
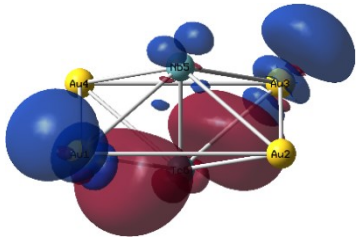
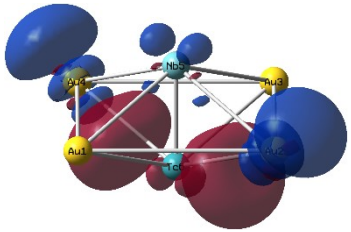
Scheme E. $^{5}[NbAu_4]^{+}$ fragment and $^{5}[Tc]^{-}$ fragment β NOCV orbitals				
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}1\beta}$ = -229.88	$\Delta E_{orb\text{-}2\beta}$ = -65.03	$\Delta E_{orb\text{-}3\beta}$ = -55.89	$\Delta E_{orb\text{-}4\beta}$ = -94.91
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}5\beta}$ = -55.05	$\Delta E_{orb\text{-}6\beta}$ = -15.08	$\Delta E_{orb\text{-}7\beta}$ = -3.08	$\Delta E_{orb\text{-}8\beta}$ = -11.41
$\Delta E(\alpha+\beta)$ = -1179.65 kcal·mol^{-1}				

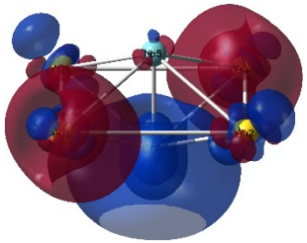
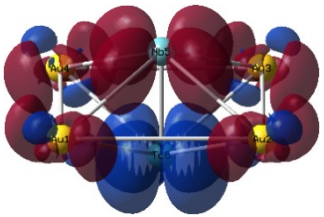
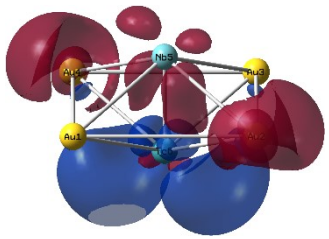
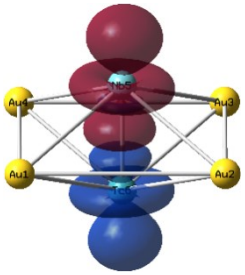
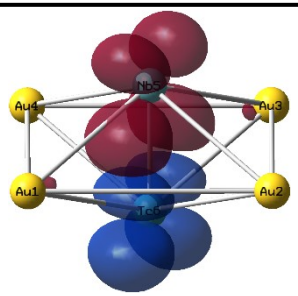
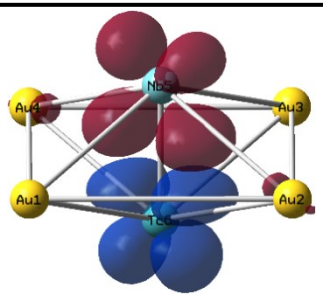
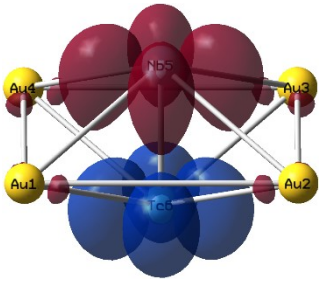
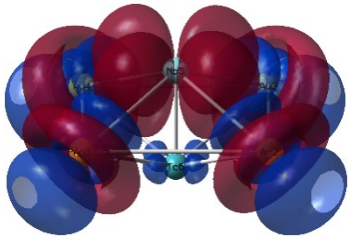
Scheme F. ^{6}[$NbAu_4$] fragment and ^{6}[Tc] fragment α NOCV orbitals				
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}1\alpha}$ = -273.13	$\Delta E_{orb\text{-}2\alpha}$ = -69.21	$\Delta E_{orb\text{-}3\alpha}$ = -128.58	$\Delta E_{orb\text{-}4\alpha}$ = -85.59
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}5\alpha}$ = -39.98	$\Delta E_{orb\text{-}6\alpha}$ = -5.97	$\Delta E_{orb\text{-}7\alpha}$ = -3.83	$\Delta E_{orb\text{-}8\alpha}$ = -1.07

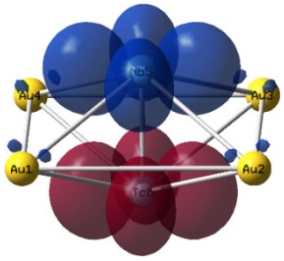
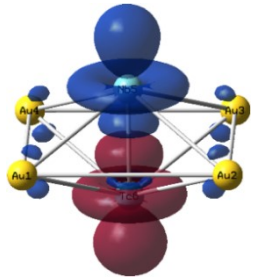
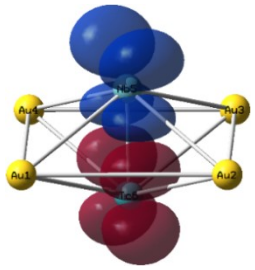
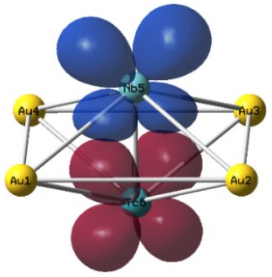
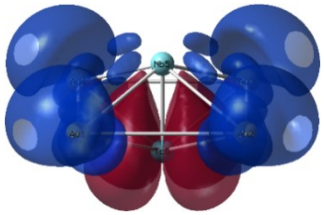
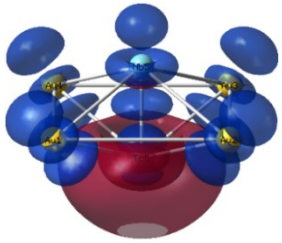
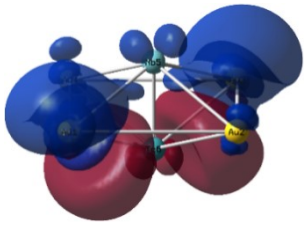
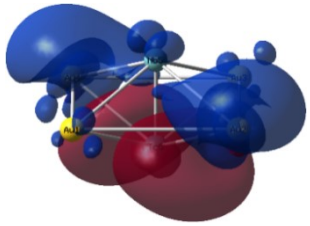
Scheme F. $^{6}[NbAu_4]$ **fragment and** $^{6}[Tc]$ **fragment β NOCV orbitals**				
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}1\beta}$ = -193.75	$\Delta E_{orb\text{-}2\beta}$ = -70.91	$\Delta E_{orb\text{-}3\beta}$ = -57.52	$\Delta_{orb\text{-}4\beta}$ = -86.93
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}5\alpha}$ = -58.07	$\Delta E_{orb\text{-}6\alpha}$ = -18.71	$\Delta E_{orb\text{-}7\alpha}$ = -1.86	$\Delta E_{orb\text{-}8\alpha}$ = -2.45
$\Delta E(\alpha+\beta)$ = -1097.56 kcal·mol^{-1}				

Scheme G. $^{7}[NbAu_4]^{+}$ **fragment and** $^{7}[Tc]^{-}$ **fragment α NOCV orbitals**				
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}1\alpha}$ = -272.44	$\Delta E_{orb\text{-}2\alpha}$ = -75.49	$\Delta E_{orb\text{-}3\alpha}$ = -118.19	$\Delta E_{orb\text{-}4\alpha}$ = -85.63
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}5\alpha}$ = -44.28	$\Delta E_{orb\text{-}6\alpha}$ = -6.19	$\Delta E_{orb\text{-}7\alpha}$ = -3.55	$\Delta E_{orb\text{-}8\alpha}$ = -13.96

Scheme G. $^{7}[NbAu_4]^{+}$ fragment and $^{7}[Tc]^{-}$ fragment β NOCV orbitals				
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}1\beta}$ = -211.48	$\Delta E_{orb\text{-}2\beta}$ = -69.78	$\Delta E_{orb\text{-}3\beta}$ = -92.36	$\Delta E_{orb\text{-}4\beta}$ = -74.16
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}5\beta}$ = -59.63	$\Delta E_{orb\text{-}6\beta}$ = -115.89	$\Delta E_{orb\text{-}7\beta}$ = -17.70	$\Delta E_{orb\text{-}8\beta}$ = -1.74
$\Delta E(\alpha+\beta)$ = -1262.47 kcal·mol^{-1}				

Scheme H. $^{8}[NbAu_4]$ **fragment and** $^{8}[Tc]$ **fragment α NOCV orbitals**				
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}1\alpha}$ = -67.27	$\Delta E_{orb\text{-}2\alpha}$ = -140.57	$\Delta E_{orb\text{-}3\alpha}$ = -85.43	$\Delta E_{orb\text{-}4\alpha}$ = -85.43
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}5\alpha}$ = -41.76	$\Delta E_{orb\text{-}6\alpha}$ = -25.75	$\Delta E_{orb\text{-}7\alpha}$ = -3.62	$\Delta E_{orb\text{-}8\alpha}$ = -3.62

Scheme H. $^{8}[NbAu_4]$ **fragment and** $^{8}[Tc]$ **fragment β NOCV orbitals**				
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}1\beta}$ = -192.23	$\Delta E_{orb\text{-}2\beta}$ = -71.03	$\Delta E_{orb\text{-}3\beta}$ = -102.11	$\Delta_{orb\text{-}4\beta}$ = -86.47
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}5\alpha}$ = -58.53	$\Delta E_{orb\text{-}6\alpha}$ = -84.96	$\Delta E_{orb\text{-}7\alpha}$ = -19.13	$\Delta E_{orb\text{-}8\alpha}$ = -2.47
$\Delta E(\alpha+\beta)$ = -1070.38 kcal·mol^{-1}				

Scheme I. $^{9}[NbAu_4]^{+}$ fragment and $^{9}[Tc]^{-}$ fragment α NOCV orbitals				
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}1\alpha}$ = -67.49	$\Delta E_{orb\text{-}2\alpha}$ = -148.79	$\Delta E_{orb\text{-}3\alpha}$ = -84.72	$\Delta E_{orb\text{-}4\alpha}$ = -84.72
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}5\alpha}$ = -40.58	$\Delta E_{orb\text{-}6\alpha}$ = -26.61	$\Delta E_{orb\text{-}7\alpha}$ = -3.42	$\Delta E_{orb\text{-}8\alpha}$ = -3.42

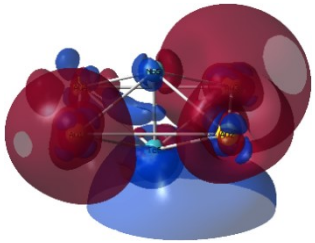
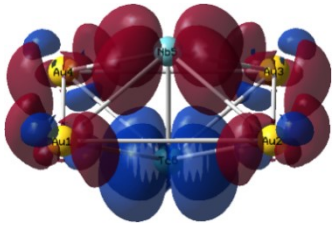
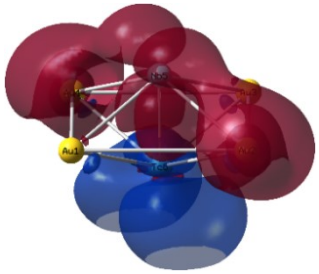
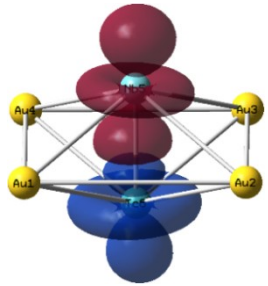
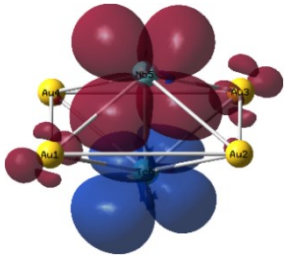
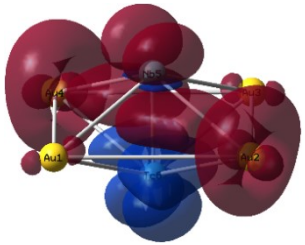
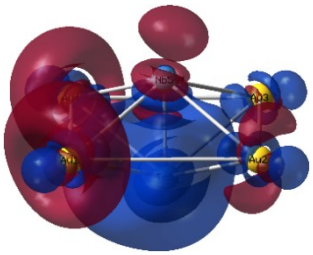
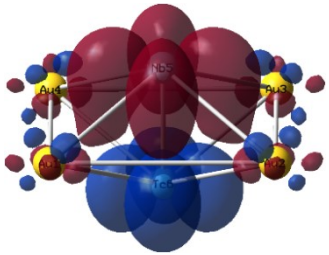
Scheme I. $^{9}[NbAu_4]^{+}$ fragment and $^{9}[Tc]^{-}$ fragment β NOCV orbitals				
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}1\beta}$ = -136.17	$\Delta E_{orb\text{-}2\beta}$ = -70.81	$\Delta E_{orb\text{-}3\beta}$ = -79.56	$\Delta E_{orb\text{-}4\beta}$ = -77.40
Diagrams				
Energy / (kcal·mol^{-1})	$\Delta E_{orb\text{-}5\beta}$ = -58.84	$\Delta E_{orb\text{-}6\beta}$ = -99.70	$\Delta E_{orb\text{-}7\beta}$ = -153.39	$\Delta E_{orb\text{-}8\beta}$ = -20.52
$\Delta E(\alpha+\beta)$ = -1156.14 kcal·mol^{-1}				

Table S30. Topological parameters from ELF analysis at the bond critical points for the D_{6h}-Nb_2Au_6, C_{4v}-$NbTcAu_4$, and D_{4h}-Mo_2Au_4 clusters.

System	D_{6h}-Nb_2Au_6	C_{4v}-$NbTcAu_4$	D_{4h}-Mo_2Au_4
G(r)	0.273	0.360	0.408
V(r)	-0.420	-0.552	-0.632

Table S31. AdNDP-based comparison of 5p orbital participation elucidating distinct bonding nature in D_{6h}-Nb_2Au_6, C_{4v}-$NbTcAu_4$ and D_{4h}-Mo_2Au_4 systems at the PBE0/Def2-TZVP level.

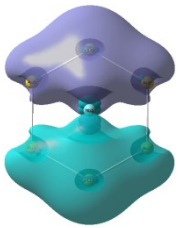
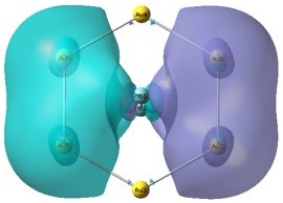
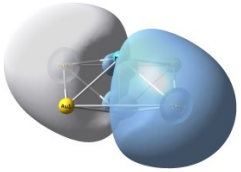
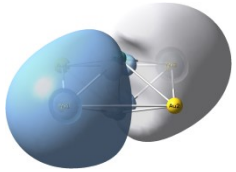
	D_{6h}-Nb_2Au_6		C_{4v}-$NbTcAu_4$		D_{4h}-Mo_2Au_4	
Diagrams						
Component	Nb_2©$5p_y$~22.5%	Nb_2©$5p_x$~22.5%	Nb©$5p_y$~16.3% Tc©$5p_y$~14.3%	Nb©$5p_x$~16.3% Tc©$5p_x$~14.3%	Mo_2©$5p_y$~31.4%	Mo_2©$5p_x$~31.4%

Table S32. Atomic charge evaluation in all-metal clusters with Au/Ag/Cu Ligands.

	NPA_{Nb} (|e|)	NPA_{Tc} (|e|)	$Mulliken_{Nb}$ (|e|)	$Mulliken_{Tc}$ (|e|)
C_{4v}-$NbTcAu_4$	0.214	-0.429	-0.201	-0.107
C_{4v}-$NbTcAg_4$	-0.176	-0.760	0.609	-0.093
C_{4v}-$NbTcCu_4$	-0.355	-0.788	0.315	0.043

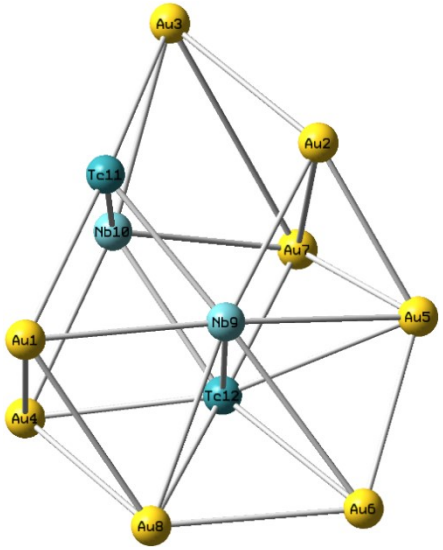
Table S33. Cartesian coordinates of C_{4v}-$NbTcAu_4$ obtained at the PBE0/Def2-TZVP level.

	Coordinate (Å) [1] **$NbTcAu_4$**		
Au	0.00000000	2.56353300	0.00376600
Au	-2.56353300	0.00000000	0.00376600
Au	0.00000000	-2.56353300	0.00376600
Au	2.56353300	0.00000000	0.00376600
Nb	0.00000000	0.00000000	0.99911700
Tc	0.00000000	0.00000000	-0.98054900

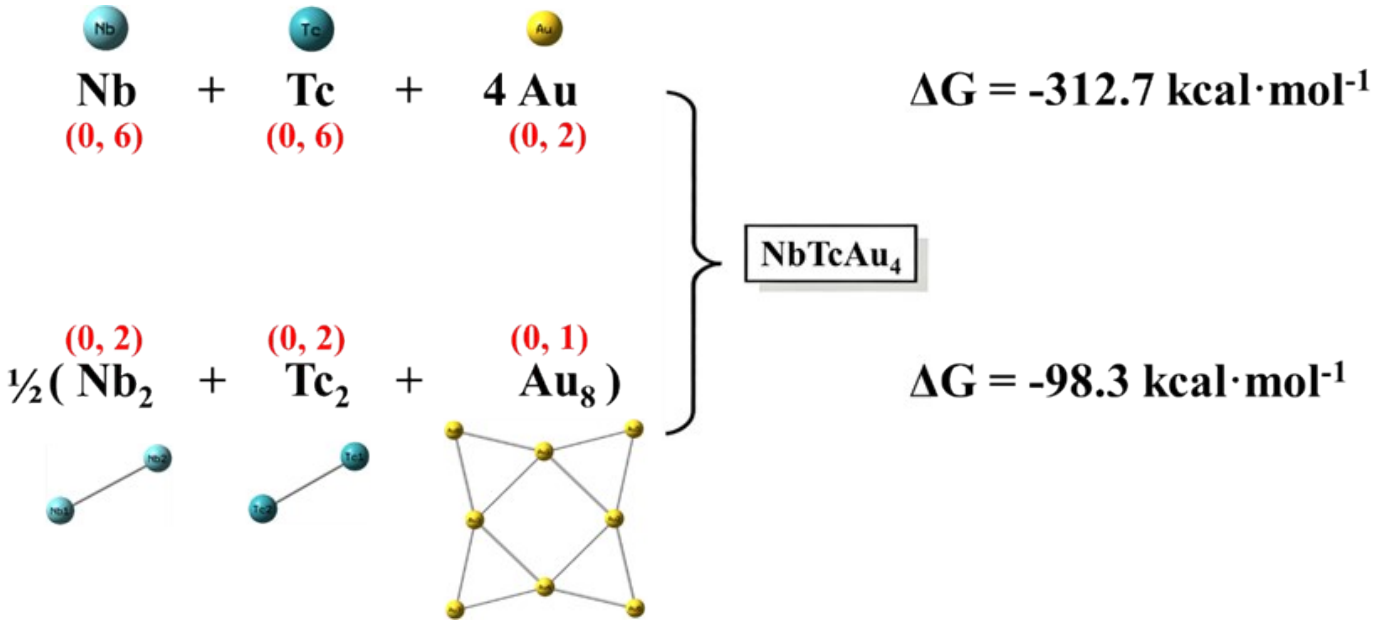
Table S34. Cartesian coordinates of D_{4h}-Mo_2Au_4 obtained at the PBE0/Def2-TZVP level.

	Coordinate (Å) [1] **Mo_2Au_4**		
Au	0.00000000	2.56353300	0.00376600
Au	-2.56353300	0.00000000	0.00376600
Au	0.00000000	-2.56353300	0.00376600
Au	2.56353300	0.00000000	0.00376600
Mo	0.00000000	0.00000000	0.99911700
Mo	0.00000000	0.00000000	-1.58088300

Table S35. Cartesian coordinates of $Nb_2Tc_2Au_8$ obtained at the PBE0/Def2-TZVP level.

Coordinate (Å) [1] $Nb_2Tc_2Au_8$				
	Au	1.20273000	2.53704800	-1.36302200
	Au	-2.17527500	-0.97263000	-1.24289700
	Au	-3.73490600	1.08312100	-0.04284500
	Au	1.48669200	2.02881900	1.70945100
	Au	-0.27581000	-2.72522100	-0.41754100
	Au	2.41777000	-2.38533300	-0.32480800
	Au	-1.48940900	-1.27604000	1.94265200
	Au	3.12534100	0.37878600	-0.21360700
	Nb	0.41167200	-0.11435200	-1.05902100
	Nb	-1.05784100	1.31426900	0.99097800
	Tc	-1.29325900	1.76097100	-1.05086700
	Tc	0.88580800	-0.45892600	1.02869400

Scheme S1. Two possible reactions and thermodynamic values for the generation of C_{4v}-$NbTcAu_4$ at the PBE0/Def2-TZVP level. The values in parentheses denote the charge and spin multiplicity (charge, multiplicity).



Scheme S2. Thermodynamic energy of dimerization reaction of C_{4v}-$NbTcAu_4$ at the PBE0/Def2-TZVP level.