Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Cage-like $Ta@B_n^q$ complexes (n=23~28, q=-1~+3) in 18-electron configurations with the highest coordination number of twenty-eight

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Figure S1. Configurational energy spectra of (a) TaB_{24}^{+}, (b) TaB_{25}, (c) TaB_{26}^{+}, and (d) TaB_{27}^{2+} at CCSD(T) level with the relative energies indicated in eV.

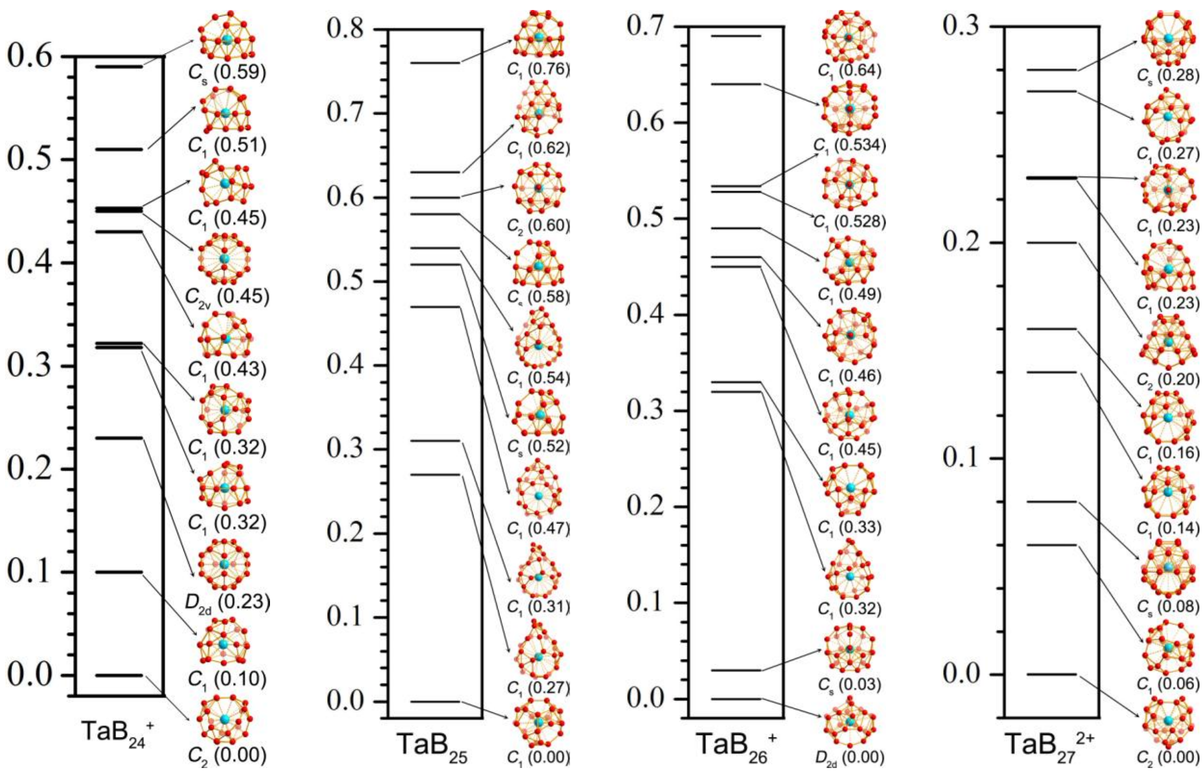

Figure S2. The three lowest-lying isomers of WB_{24} at CCSD(T) level with their relative energies indicated in eV**.**

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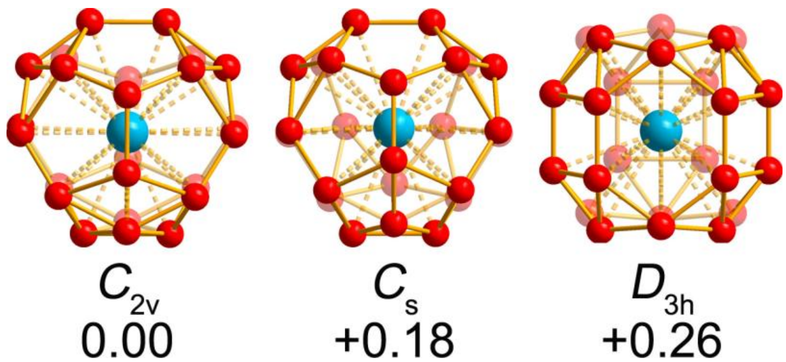


Figure S3. Molecular dynamics simulations of C_{2v} Ta@B_{24}^{-} (**4**) at 400K and 450K for 30 ps, with the root-mean-square-deviation (RMSD) and maximum bond length deviation (MAXD) values (on average) indicated in Å.

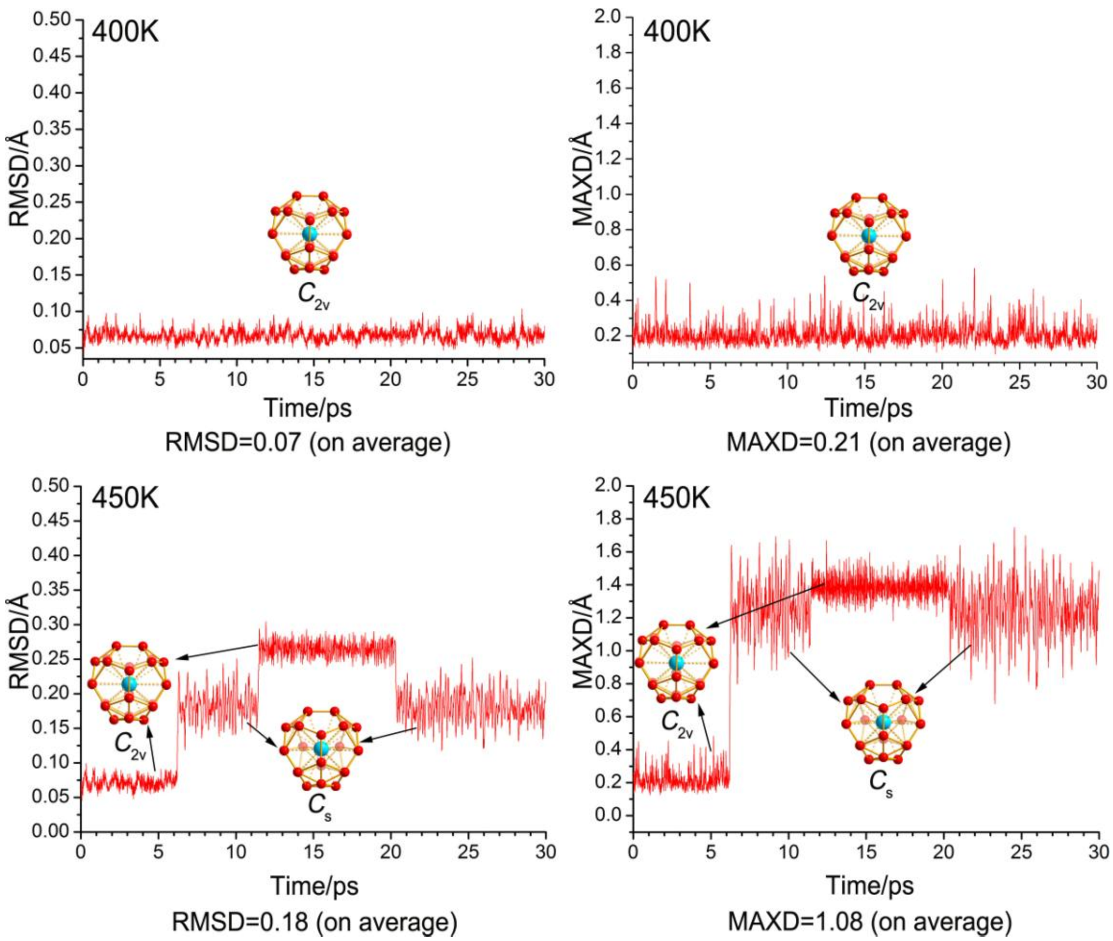


Figure S4. Low-lying isomers of TaB_{29}^{4+} at CCSD(T) level with their relative energies indicated in eV.

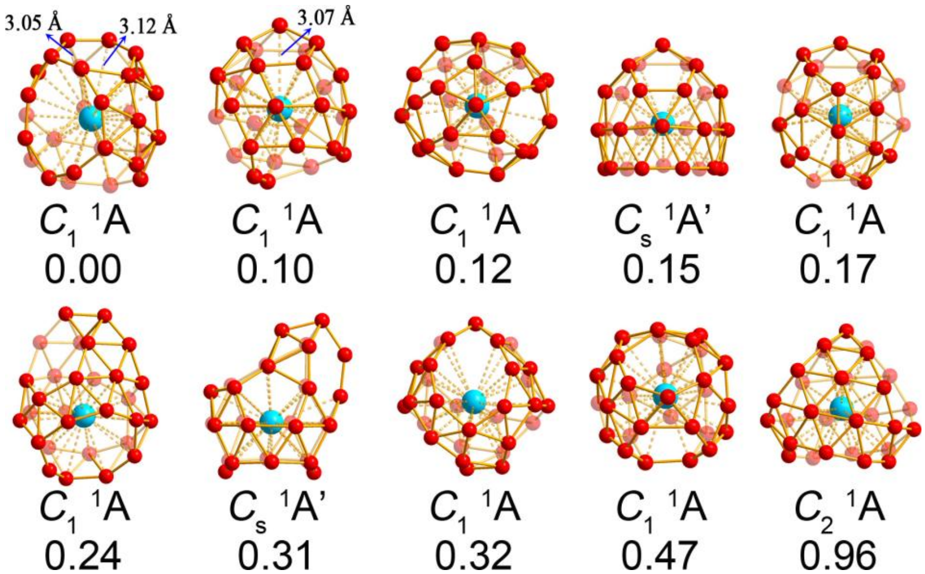


Figure S5. Variation of the coordination numbers of transition-metal-centered boron complexes M@B_n in different charge states in the size range between n=8-29.

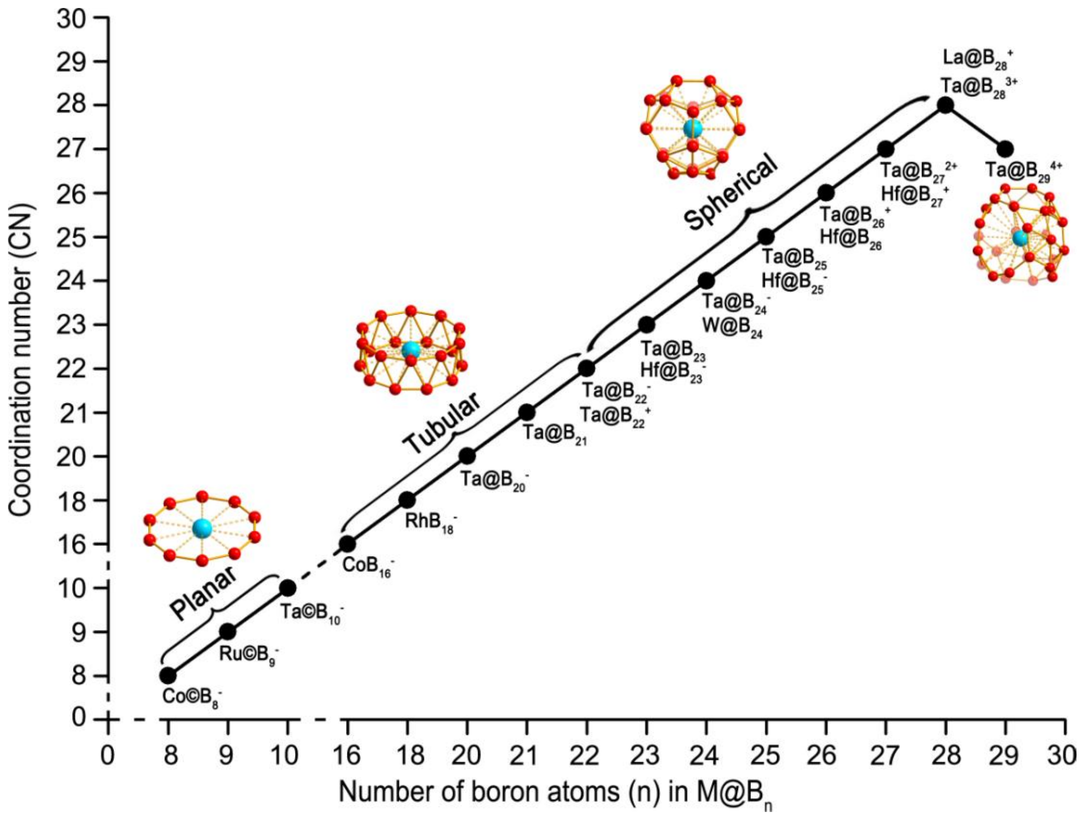
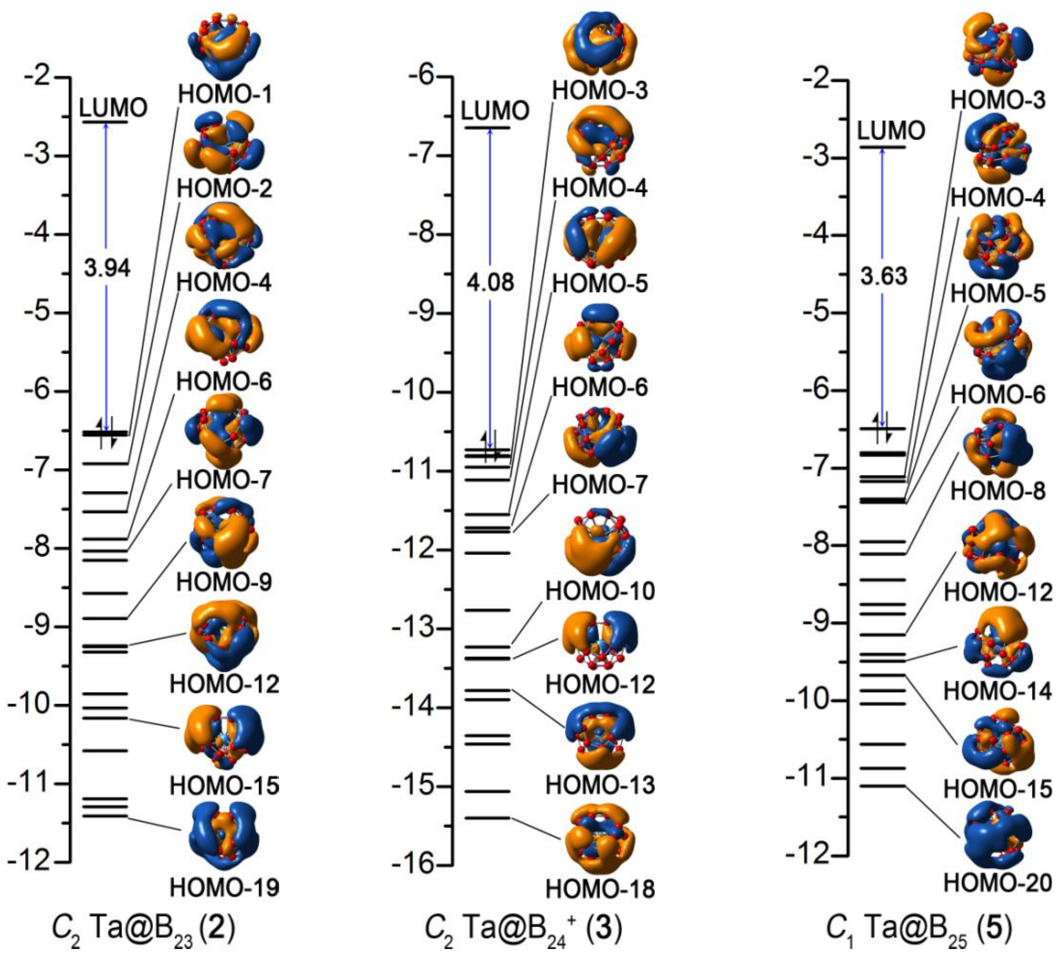


Figure S6. Eigenvalue spectra of Ta@B_{23}(**2**), Ta@B_{24}^{+}(**3**), Ta@B_{25} (**5**), Ta@B_{26}^{+} (**6**), Ta@B_{27}^{2+}(**7**), and Ta@B_{28}^{3+} (**8**).



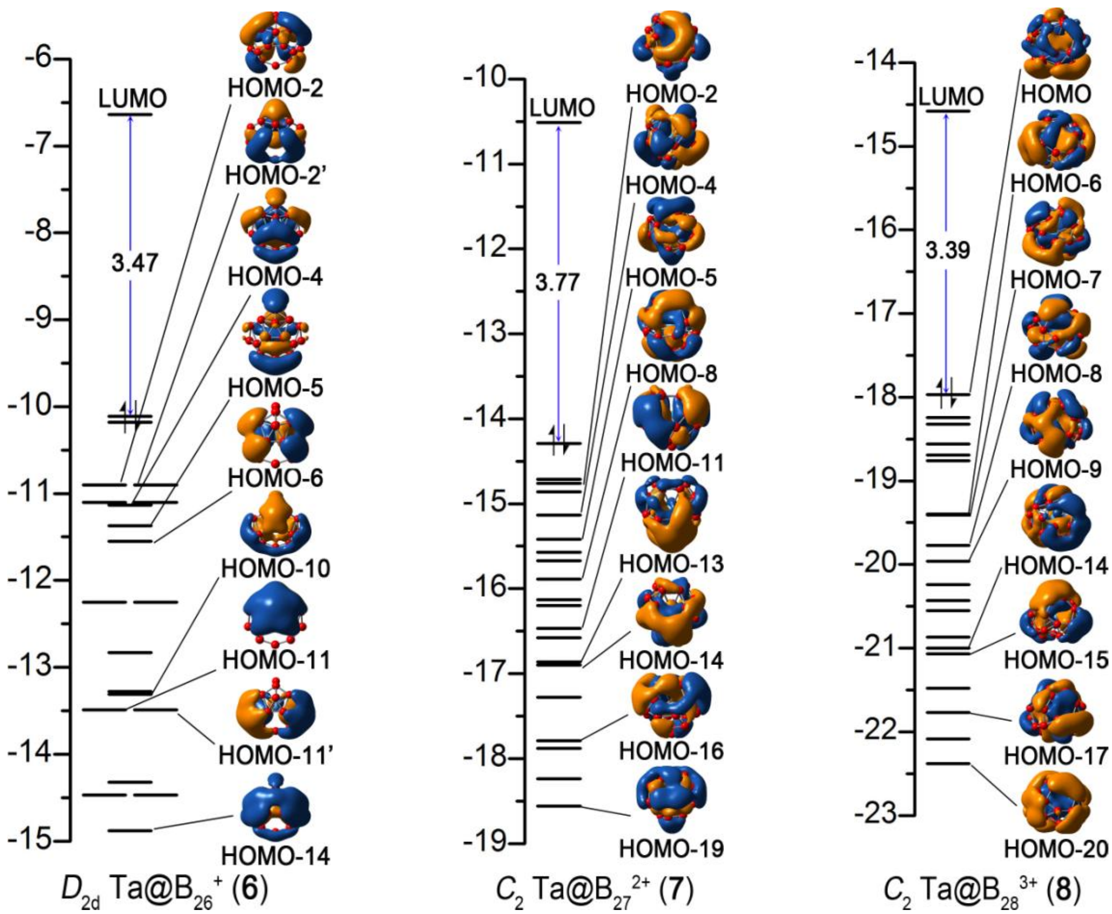
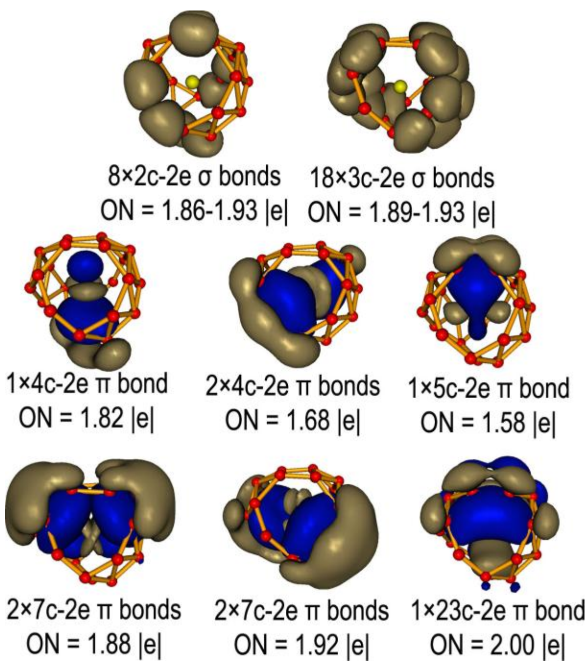
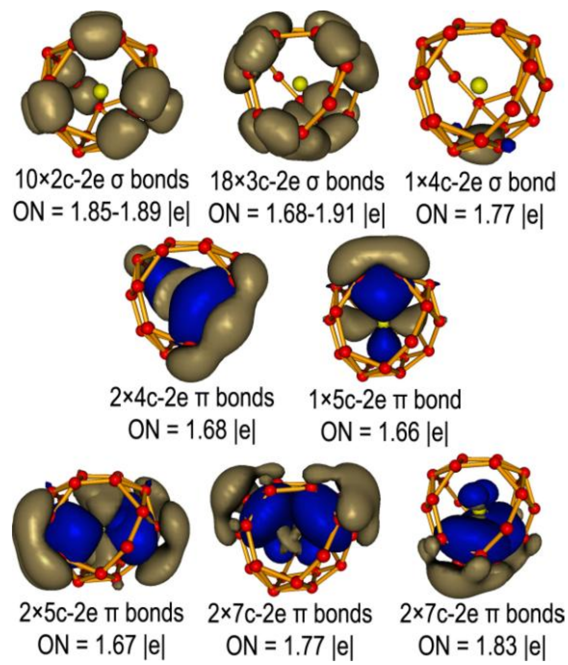

LUMO
3.47
HOMO-2
HOMO-2'
HOMO-4
HOMO-5
HOMO-6
HOMO-10
HOMO-11
HOMO-11'
HOMO-14
D_{2d} $Ta@B_{26}^{+}$ (**6**)
LUMO
3.77
HOMO-2
HOMO-4
HOMO-5
HOMO-8
HOMO-11
HOMO-13
HOMO-14
HOMO-16
HOMO-19
C_2 $Ta@B_{27}^{2+}$ (**7**)
LUMO
3.39
HOMO
HOMO-6
HOMO-7
HOMO-8
HOMO-9
HOMO-14
HOMO-15
HOMO-17
HOMO-20
C_2 $Ta@B_{28}^{3+}$ (**8**)

Figure S7. AdNDP bonding patterns of (a) $Ta@B_{23}$(**2**), (b) $Ta@B_{24}^{+}$(**3**), (c) $Ta@B_{24}^{-}$ (**4**), (d) $Ta@B_{25}$ (**5**), (e) $Ta@B_{26}^{+}$ (**6**), (f) $Ta@B_{25}$ (**7**), and (g)$Ta@B_{28}^{3+}$ (**8**).

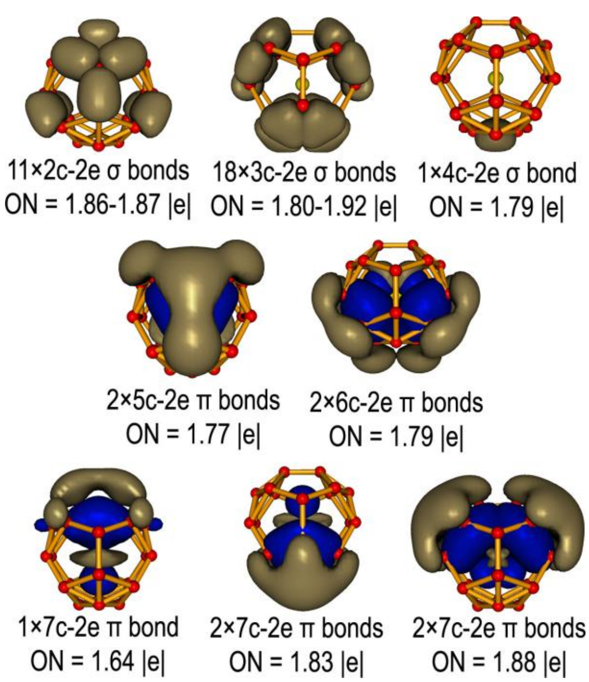
(a) C_2 $Ta@B_{23}$ (**2**)



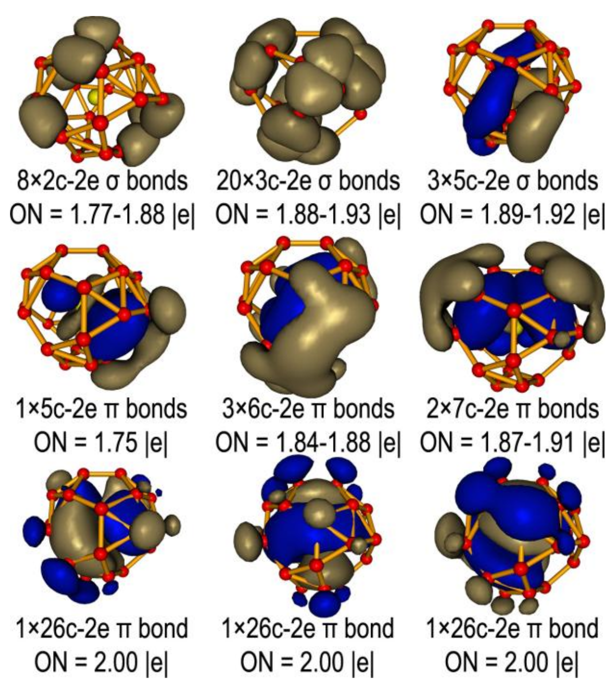
(b) C_2 $Ta@B_{24}^{+}$ (**3**)



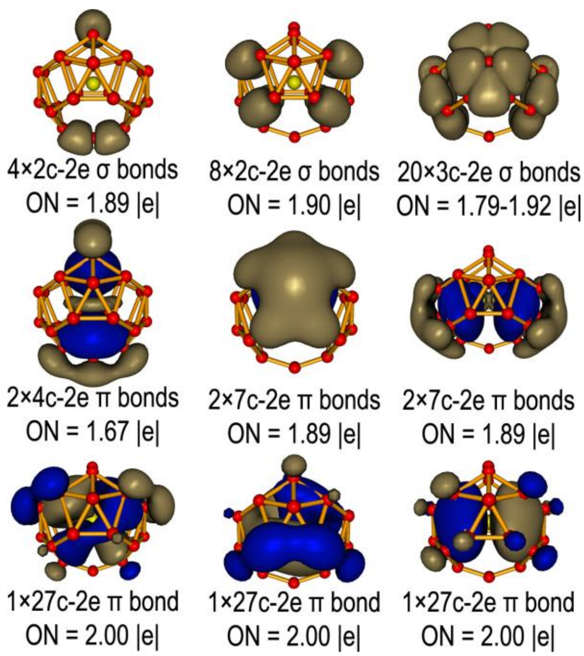
(c) C_{2v} $Ta@B_{24}^{-}$ (**4**)



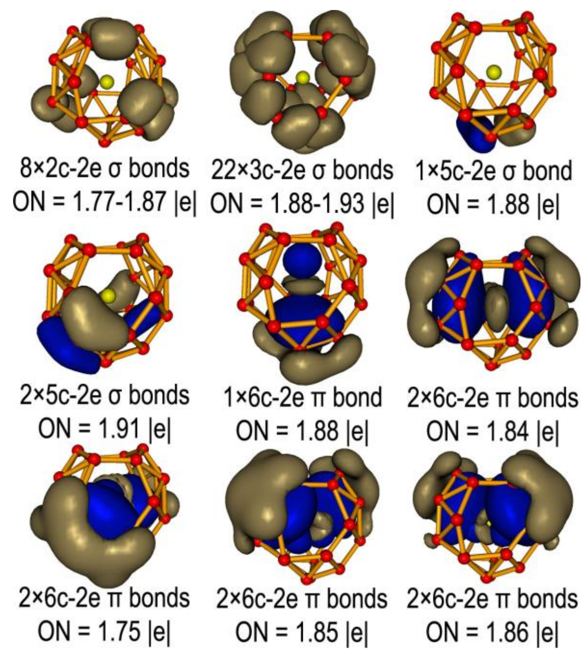
(d) C_1 $Ta@B_{25}$ (**5**)



(e) D_{2d} $Ta@B_{26}^{+}$ (**6**)



(f) C_2 $Ta@B_{27}^{2+}$ (**7**)



(g) C_2 $Ta@B_{28}^{3+}$ (**8**)

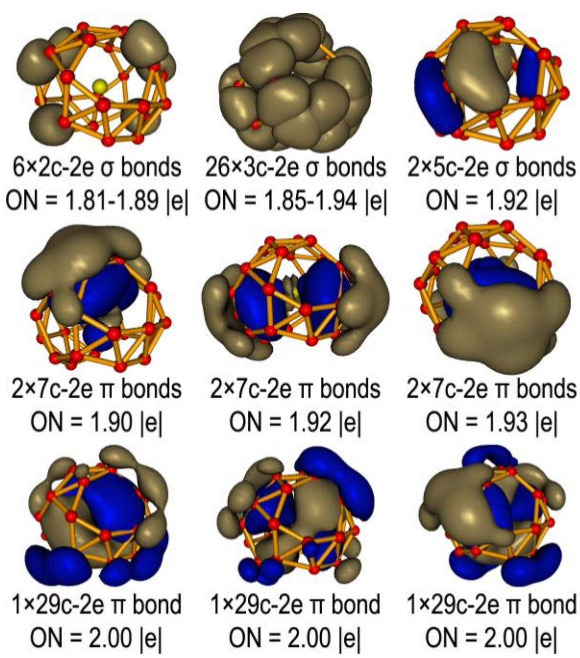


Figure S8. Simulated (a) IR, (b) Raman, and (c) UV-vis spectra of $Ta@B_{23}$(2), $Ta@B_{24}^{+}$(3), $Ta@B_{25}$ (5), $Ta@B_{26}^{+}$ (6), $Ta@B_{27}^{2+}$(7), and $Ta@B_{28}^{3+}$ (8) at PBE0 level.

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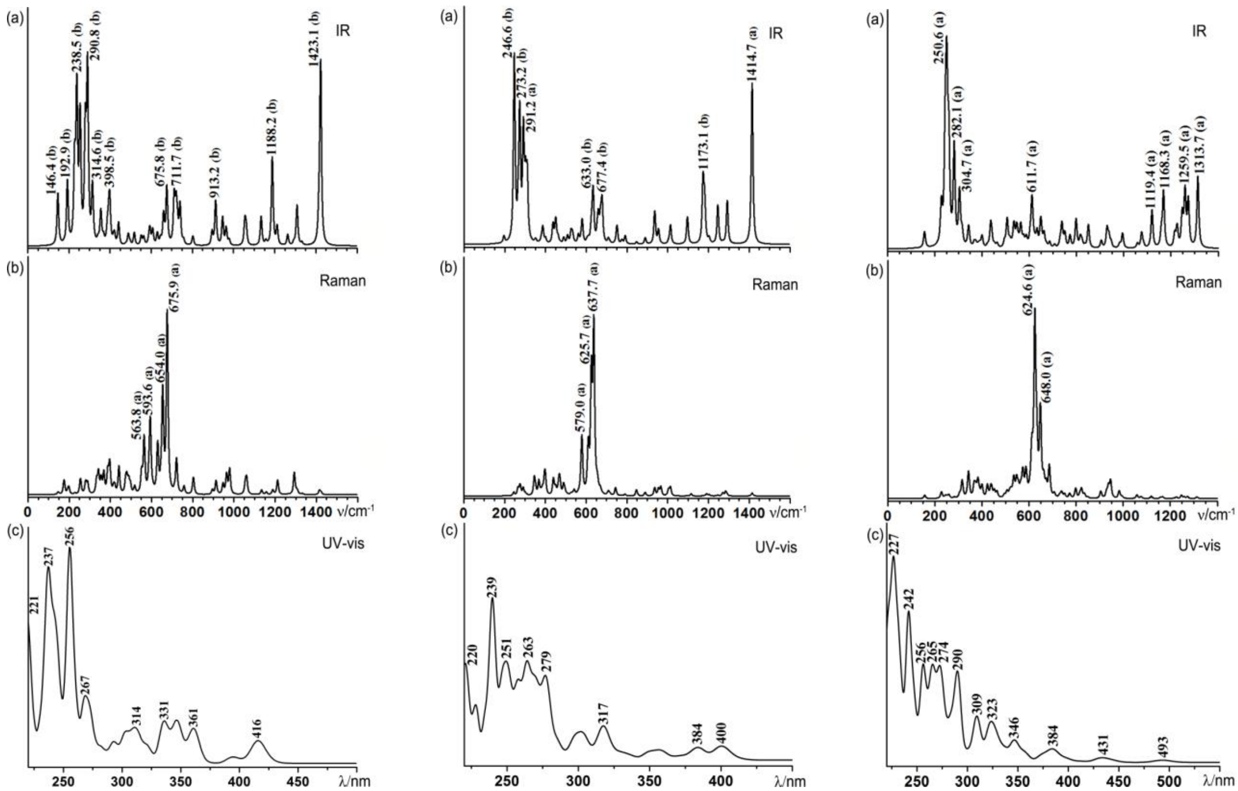
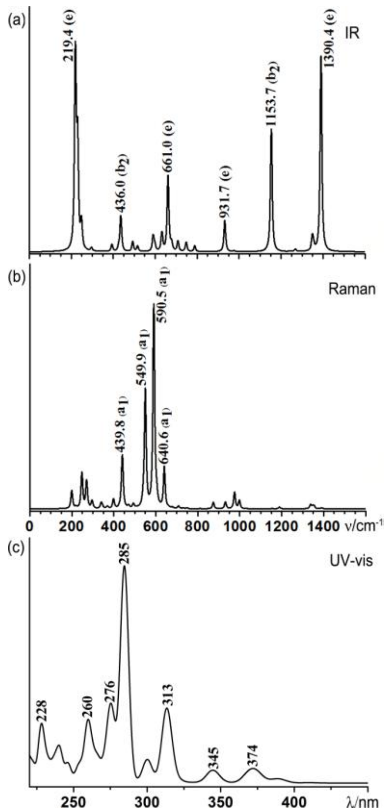
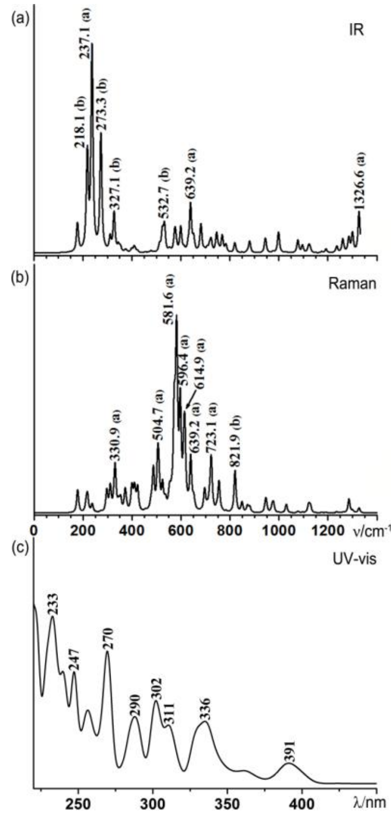


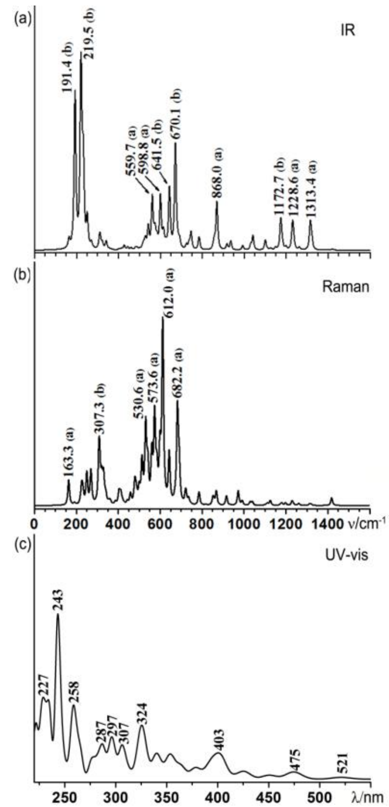
C_2 Ta@B_{23} (**2**) C_2 Ta@B_{24}^{+} (**3**) C_1 Ta@B_{25} (**5**)



D_{2d} Ta@B_{26}^{+} (**6**)



C_2 Ta@B_{27}^{2+} (**7**)



C_2 Ta@B_{28}^{3+} (**8**)

Table S1. HOMO-LUMO energy gaps (ΔE_{Gap}), minimum (r_{min}), maximum (r_{max}), and average (r_{av}) Ta-B distances, average Ta-B Wiberg bond orders (BO_{av}), total Wiberg bond orders (BO_{Ta}), natural atomic charges (q_{Ta}), and electronic configurations of the Ta centers in the endoheral metalloborospherene family **1-8** (n=22-28).

Ta@B_n	ΔE_{Gap}/eV	r_{min}/Å	r_{max}/Å	r_{av}/Å	WBI_{av}	WBI_{Ta}	q_{Ta}/|e|	electronic configuration
Ta@B_{22}^- (**1**)	3.60	2.40	2.52	2.48	0.27	5.91	-0.05	Ta[$5d^{4.54}6s^{0.27}$]
Ta@B_{23} (**2**)	3.94	2.40	2.64	2.53	0.26	5.91	-0.14	Ta[$5d^{4.64}6s^{0.27}$]
Ta@B_{24}^+(**3**)	4.08	2.38	2.62	2.51	0.26	6.12	-0.37	Ta[$5d^{4.74}6s^{0.35}$]
Ta@B_{24}^-(**4**)	3.86	2.39	2.53	2.47	0.26	6.33	-0.64	Ta[$5d^{4.91}6s^{0.43}$]
Ta@B_{25} (**5**)	3.63	2.42	2.66	2.53	0.25	6.20	-0.49	Ta[$5d^{4.82}6s^{0.42}$]
Ta@B_{26}^+(**6**)	3.47	2.60	2.74	2.64	0.23	5.97	-0.31	Ta[$5d^{4.76}6s^{0.34}$]
Ta@B_{27}^{2+}(**7**)	3.78	2.48	2.80	2.61	0.23	6.22	-0.49	Ta[$5d^{4.78}6s^{0.45}$]
Ta@B_{28}^{3+} (**8**)	3.39	2.50	2.92	2.68	0.22	6.09	-0.44	Ta[$5d^{4.79}6s^{0.43}$]

Table S2. Optimized geometries and coordinates at PBE0 level.

D_2 Ta@B_{22}^- (**1**)

B	1.90907700	1.24183800	-0.74354600
B	0.45462300	2.36796300	-0.64570500
B	0.00000000	0.00000000	-2.48080400
B	0.72663000	1.46560100	-1.91135700
B	-2.32627500	0.54007700	-0.66610300
B	-1.54638700	0.00033900	-1.95141200
B	-0.45462300	2.36796300	0.64570500
B	-0.72663000	1.46560100	1.91135700
B	-1.90907700	1.24183800	0.74354600
B	-0.72663000	-1.46560100	-1.91135700
B	-1.90907700	-1.24183800	-0.74354600
B	2.32627500	-0.54007700	-0.66610300
B	1.54638700	-0.00033900	-1.95141200
B	1.54638700	0.00033900	1.95141200
B	2.32627500	0.54007700	0.66610300
B	-2.32627500	-0.54007700	0.66610300
B	-1.54638700	-0.00033900	1.95141200
B	0.00000000	0.00000000	2.48080400
Ta	0.00000000	0.00000000	0.00000000
B	-0.45462300	-2.36796300	-0.64570500
B	1.90907700	-1.24183800	0.74354600
B	0.72663000	-1.46560100	1.91135700
B	0.45462300	-2.36796300	0.64570500

C_2 Ta@B_{23} (**2**)

B	-0.62210100	2.20434000	-0.66033300
B	-2.16555100	0.58572100	1.43898400
B	-1.17921400	-0.36996400	-2.08162500
B	-0.76469300	-1.85332600	-1.59903000
B	0.00000000	0.00000000	2.53504800
B	2.12562000	1.21170000	-0.91500500
B	-1.58988500	1.84498700	0.66590200
B	-2.54476600	-0.49336600	0.40195500
B	0.00000000	-2.32869900	1.03567100
B	1.13798200	2.25840200	-0.02436500
B	1.58988500	-1.84498700	0.66590200
B	0.65876900	-1.15741700	-1.99053000
B	0.00000000	2.32869900	1.03567100
B	0.77381300	-1.29268700	2.09717300
B	-2.12562000	-1.21170000	-0.91500500
B	-0.65876900	1.15741700	-1.99053000
B	2.16555100	-0.58572100	1.43898400
B	1.17921400	0.36996400	-2.08162500
B	0.76469300	1.85332600	-1.59903000
B	0.62210100	-2.20434000	-0.66033300
B	-0.77381300	1.29268700	2.09717300
B	2.54476600	0.49336600	0.40195500
Ta	0.00000000	0.00000000	0.04981900
B	-1.13798200	-2.25840200	-0.02436500

C_2 Ta@B_{24}^{+} (**3**)

B	-0.66343500	0.65586600	-2.18112800
B	0.00000000	2.11198900	-1.33322800
B	2.03582000	0.01171500	-1.43605600
B	0.97733900	1.04250100	-2.09315200
B	2.43988300	-0.42365900	0.07068400
B	2.02043200	-0.17806600	1.62873100
B	-1.02150500	2.40315100	-0.17506000
B	-1.70408900	1.69297900	1.01455500
B	0.93074800	0.96814700	2.13077700
B	-0.93074800	-0.96814700	2.13077700
B	1.70408900	-1.69297900	1.01455500
B	-0.97733900	-1.04250100	-2.09315200
B	0.66343500	-0.65586600	-2.18112800
B	-2.43988300	0.42365900	0.07068400
B	-2.03582000	-0.01171500	-1.43605600
B	0.69418900	-0.97144200	2.20399800
B	-0.69418900	0.97144200	2.20399800
B	-2.02043200	0.17806600	1.62873100
Ta	0.00000000	0.00000000	0.01017300
B	1.02150500	-2.40315100	-0.17506000
B	-1.58245200	-1.71105300	-0.73465400
B	-1.91116100	-1.30679800	0.83026900
B	0.00000000	-2.11198900	-1.33322800
B	1.58245200	1.71105300	-0.73465400
B	1.91116100	1.30679800	0.83026900

C_{2v} Ta@B_{24}^{-} (**4**)

B	1.46728200	1.43555000	1.30372000
B	0.00000000	1.40090400	2.05005100
B	-1.37259000	-1.47439200	-1.45841100
B	1.46728200	-1.43555000	1.30372000
B	0.00000000	-2.35618000	0.74159600
B	0.00000000	-1.40090400	2.05005100
B	-2.12037600	0.00000000	-1.38135900
B	-0.82093500	0.00000000	-2.35453500
B	0.00000000	2.31283200	-0.94721000
B	0.82093500	0.00000000	-2.35453500
B	1.37259000	1.47439200	-1.45841100
B	2.12037600	0.00000000	-1.38135900
B	0.00000000	-2.31283200	-0.94721000
B	-1.46728200	1.43555000	1.30372000
B	-1.37259000	1.47439200	-1.45841100
B	0.00000000	2.35618000	0.74159600
B	1.37259000	-1.47439200	-1.45841100
B	2.29445300	-0.89959300	-0.01435700
B	0.92295300	0.00000000	2.21097600
B	-2.29445300	-0.89959300	-0.01435700
B	-0.92295300	0.00000000	2.21097600
B	2.29445300	0.89959300	-0.01435700
B	-1.46728200	-1.43555000	1.30372000
B	-2.29445300	0.89959300	-0.01435700
Ta	0.00000000	0.00000000	0.00254500

C_1 Ta@B_{25} (**5**)

B	-2.22849200	1.41535400	0.09143000
B	-1.79709500	0.65249500	-1.48606300
B	1.61226300	2.08124700	0.07873400
B	0.04609500	2.48574000	0.46471100
B	2.11479100	-0.40346800	-1.37167500
B	2.47684500	0.67105300	-0.21687800
B	-2.60249300	-0.11733300	-0.19688300
B	-0.40123900	-1.71480100	-1.73468700
B	0.65621600	-0.33907900	-2.30511600
B	1.96466400	1.03475400	1.31330300
B	1.88859100	-1.70618500	-0.03794600
B	-1.15961500	1.77616500	1.36004600
B	1.03869300	0.10712200	2.30040300
B	-2.10628000	-1.53183200	0.43717100
B	-1.53413300	-0.92037600	1.79758600
B	1.18481900	-1.72634200	-1.52235900
B	0.38089200	-2.44251200	-0.24282100
B	-1.83714800	-1.15080500	-1.24714000
Ta	0.01268800	-0.00695200	0.00390600
B	2.15319300	-0.58260000	1.10435300
B	-0.65673000	0.46641400	2.31728000
B	-0.65915600	-2.18415500	1.02425700
B	0.02348900	-1.12271000	2.24101200
B	-1.04935300	2.05801300	-0.92868600
B	-0.23158100	1.07308100	-2.14953100
B	0.53751800	2.22226000	-1.14752800

D_{2d} $Ta@B_{26}^{+}$ (**6**)

B	-0.81654500	2.47245300	0.56192900
B	0.00000000	2.58995600	-0.88822200
B	0.00000000	-2.58995600	-0.88822200
B	2.47245300	0.81654500	-0.56192900
B	2.47245300	-0.81654500	-0.56192900
B	1.40428800	1.84409800	-1.18832800
B	-2.47245300	-0.81654500	-0.56192900
B	-0.81654500	-2.47245300	0.56192900
B	-1.48638800	0.00000000	2.13558400
B	0.00000000	0.00000000	2.62108500
B	-1.84409800	-1.40428800	1.18832800
B	1.84409800	-1.40428800	1.18832800
B	1.40428800	-1.84409800	-1.18832800
B	-2.58995600	0.00000000	0.88822200
B	-2.47245300	0.81654500	-0.56192900
B	-1.84409800	1.40428800	1.18832800
B	0.81654500	-2.47245300	0.56192900
B	1.84409800	1.40428800	1.18832800
B	0.81654500	2.47245300	0.56192900
B	0.00000000	0.00000000	-2.62108500
B	-1.40428800	1.84409800	-1.18832800
B	1.48638800	0.00000000	2.13558400
B	0.00000000	-1.48638800	-2.13558400
B	-1.40428800	-1.84409800	-1.18832800
Ta	0.00000000	0.00000000	0.00000000
B	0.00000000	1.48638800	-2.13558400
B	2.58995600	0.00000000	0.88822200

C_2 Ta@B_{27}^{2+} (**7**)

B	2.51508900	0.89667300	0.48328300
B	0.17704000	1.72140000	1.84915200
B	2.34707600	1.06456400	-1.09424500
B	1.57364200	0.79275300	1.91400400
B	-1.52540000	1.79135500	-0.79412400
B	-1.16069400	0.83482100	2.25242900
B	0.38698300	-1.54447100	-1.97028400
B	1.27785600	-1.93622500	0.98808000
B	-0.17704000	-1.72140000	1.84915200
B	1.00784200	2.13849800	-0.99556300
B	-0.38698300	1.54447100	-1.97028400
B	-1.27785600	1.93622500	0.98808000
B	2.55175500	-0.50419700	-0.51096700
B	-1.15308100	-1.04361000	-2.20992800
B	1.52540000	-1.79135500	-0.79412400
B	0.00000000	2.49406400	0.22086400
B	-2.55175500	0.50419700	-0.51096700
B	0.00000000	-2.49406400	0.22086400
B	1.16069400	-0.83482100	2.25242900
B	-1.57364200	-0.79275300	1.91400400
B	1.15308100	1.04361000	-2.20992800
B	2.34004800	-0.55494900	1.18557500
B	-2.34707600	-1.06456400	-1.09424500
B	-2.51508900	-0.89667300	0.48328300
B	-1.00784200	-2.13849800	-0.99556300
B	-2.34004800	0.55494900	1.18557500
B	0.00000000	0.00000000	-2.65164300
Ta	0.00000000	0.00000000	0.00103400

C_2 Ta@B_{28}^{3+} (**8**)

B	1.34638600	-1.99635800	1.24398100
B	-1.91642600	1.36531800	-1.29459900
B	0.23766000	1.84982400	1.94702300
B	-1.46872400	-0.85279000	2.04221500
B	-1.24212300	2.61106400	-0.38333900
B	0.91143200	1.20503800	-2.07107000
B	2.53897800	0.88079100	0.68683000
B	-1.98896600	-1.38327000	-0.81758600
B	-0.69561800	0.49585500	-2.30401100
B	1.46872400	0.85279000	2.04221500
B	-0.91143200	-1.20503800	-2.07107000
B	2.61735000	-0.23225100	-0.40182100
B	2.13029100	-0.55614300	1.43247500
B	1.47915500	2.11612400	0.68773100
B	1.24212300	-2.61106400	-0.38333900
B	0.69561800	-0.49585500	-2.30401100
B	-1.47915500	-2.11612400	0.68773100
B	0.00000000	-2.78261000	0.58528800
B	1.98896600	1.38327000	-0.81758600
B	-2.61735000	0.23225100	-0.40182100
B	0.00000000	2.78261000	0.58528800
B	-1.34638600	1.99635800	1.24398100
B	-0.23766000	-1.84982400	1.94702300
B	-2.13029100	0.55614300	1.43247500
B	0.47704200	-2.03741400	-1.72136300
B	1.91642600	-1.36531800	-1.29459900
B	-0.47704200	2.03741400	-1.72136300
B	-2.53897800	-0.88079100	0.68683000
Ta	0.00000000	0.00000000	0.05044500

C_1 Ta@B_{29}^{4+}

B	2.47407300	0.05257200	1.44104700
B	-1.69360800	-0.50675300	-2.12483700
B	-2.91597800	0.72252900	0.11802900
B	-1.29767700	-1.97006500	-1.11383000
B	-1.97564500	0.85362400	1.52848300
B	0.38850300	-2.21439300	-1.18524000
B	1.30817700	-1.17798000	-2.22501700
B	2.20778700	1.40020000	0.60275800
B	-0.35795500	2.54372400	-0.09107500
B	1.35202900	-1.13527100	1.95290800
B	-0.36472300	-1.27434000	-2.42750000
B	-2.79878000	-0.56466500	1.08054400
B	-1.44384300	-1.29228800	1.75563000
B	-0.98478500	1.83576100	-1.68842400
B	0.55946100	2.03187500	1.28529300
B	-0.50728000	1.08300100	2.26652600
B	1.28904200	2.50484600	-0.12510600
B	-0.13823000	-0.64329400	2.51921200
B	0.98936200	-2.32769900	0.55177600
B	-1.87015900	1.90455100	-0.15677200
B	2.42042800	-1.41773500	0.68583000
B	1.04100900	0.53312400	2.24233500
B	2.05268600	0.20488800	-2.04667100
B	1.95180700	-1.84652500	-0.79780100
B	0.56311500	2.14710000	-1.60145500
B	-2.14441000	-1.84456100	0.29508100
B	2.09597100	1.52041500	-1.18544600
B	-2.30893700	0.85922300	-1.46424200
B	-0.63589100	-2.40802600	0.52231300
Ta	0.05099000	0.02918900	-0.04207900