

Supporting Information

Perfect tubular Ta@B₁₈³⁻, Ta₂@B₁₈, and Ta₂@B₂₇⁺ as embryos of α -boronanotubes with a transition-metal wire coordinated inside†

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Figure S1 Configurational energy spectra of (a) TaB_{18}^{3-} , (b) $\text{Ta}_2\text{@B}_{18}$, and (c) $\text{Ta}_2\text{@B}_{27}^+$ at PBE0 level, with the relative energies including zero-point corrections indicated, (T) represents triplet.

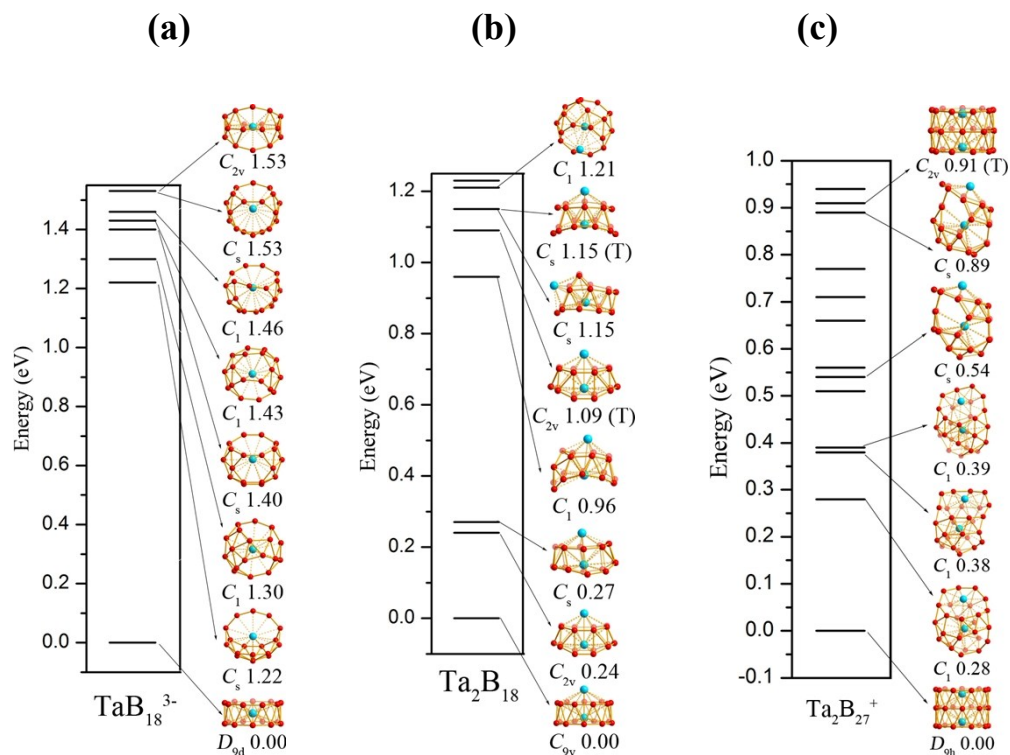
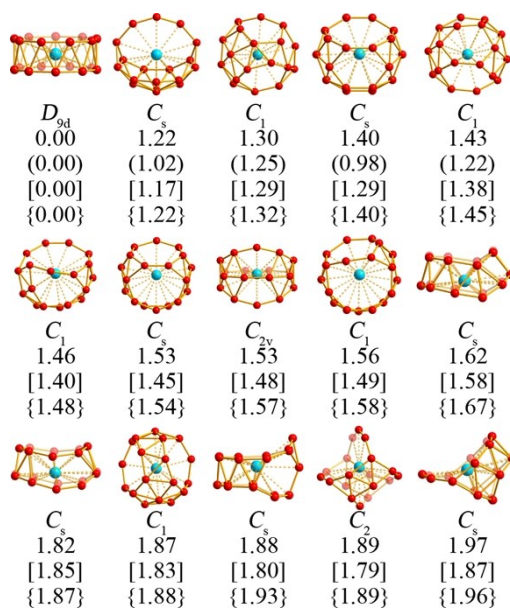
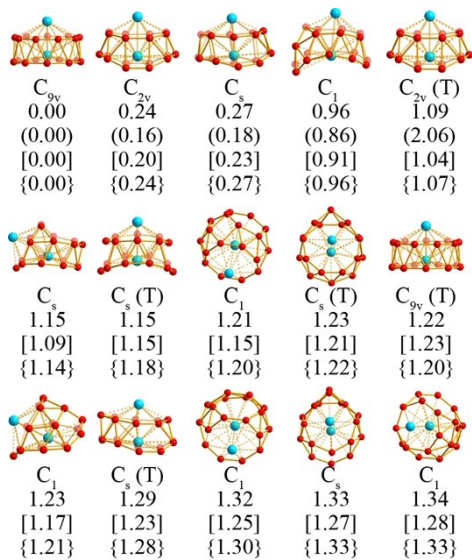


Figure S2 Relative energies of low-lying isomers of (a) TaB_{18}^{3-} , (b) Ta_2B_{18} , and (c) $\text{Ta}_2\text{B}_{27}^+$ at PBE0, CCSD(T) (parenthesis), TPSSh (square brackets), and HSE06 (curly braces) levels, (T) represents triplet.

(a) TaB_{18}^{3-}



(b) Ta_2B_{18}



(c) $Ta_2B_{27}^+$

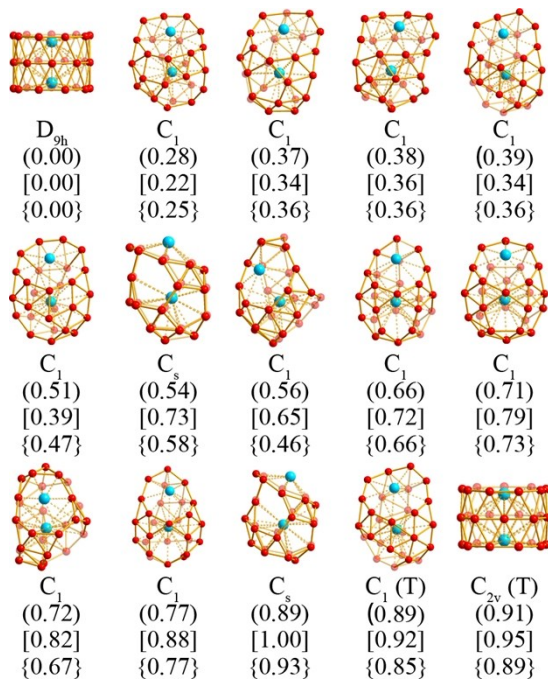


Figure S3 optimized structures of D_{9h} $V_2@B_{27}^+$, D_{9h} $Nb_2@B_{27}^+$, and D_{9h} $Hf_2@B_{27}^-$ at PBE0 level.

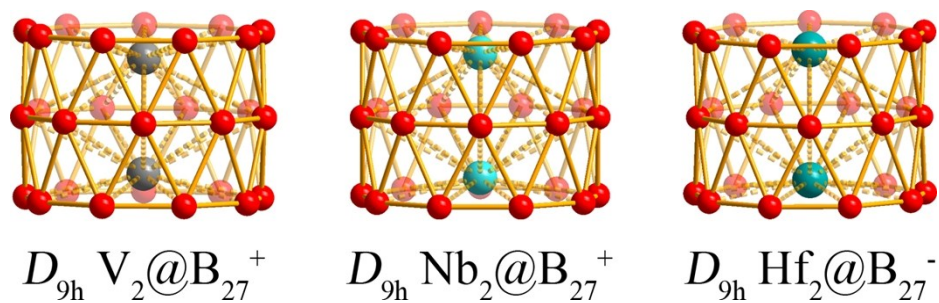


Figure S4 Optimized structures of TRT D_{8h} $\text{Cr}_2@\text{B}_{24}$ and TRT D_{2h} $\text{Zr}_2@\text{B}_{30}^{2+}$ and their configurational energy spectra at PBE0 level.

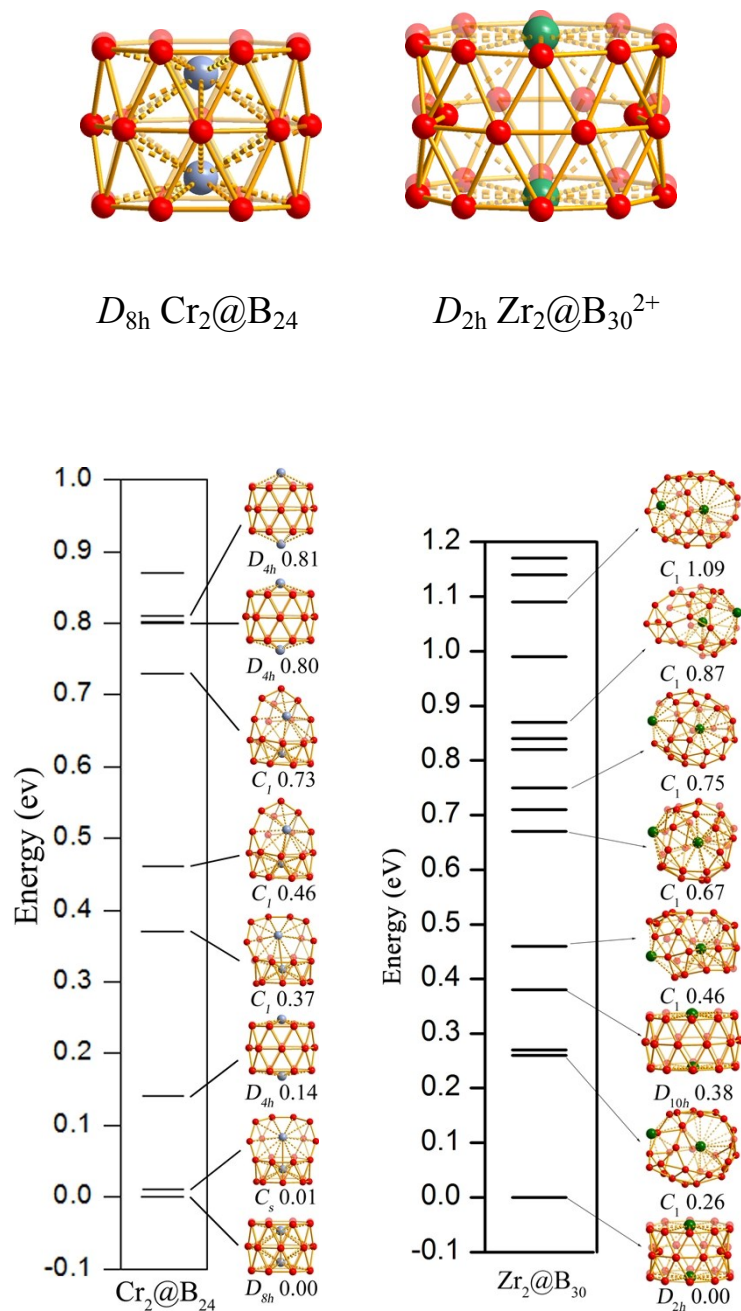


Figure S5 optimized structures of (a) D_{3h} $\text{Ta}_3@\text{B}_{42}^-$, (b) C_{3v} $\text{Ta}_3@\text{B}_{42}^+$, (c) and (d) D_{3h} $\text{Hf}_3@\text{B}_{42}$ at PBE0 level.

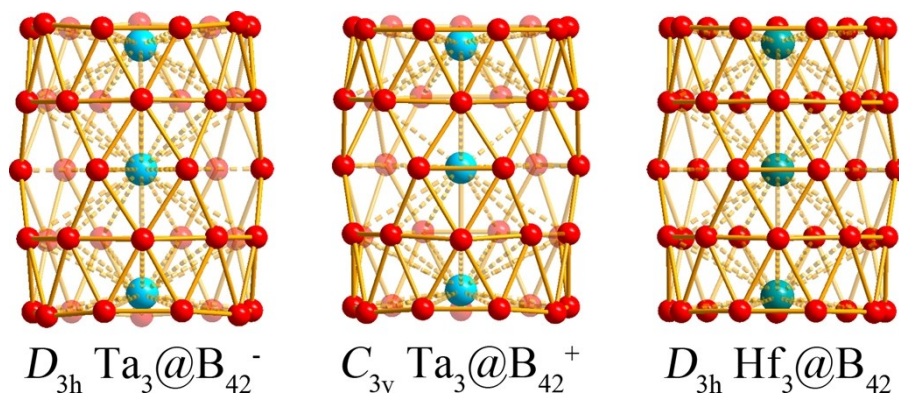


Figure S6 AdNDP bonding patterns of (a) D_{8h} $\text{Cr}_2@\text{B}_{24}$ and (b) D_{2h} $\text{Zr}_2@\text{B}_{30}^{2+}$.

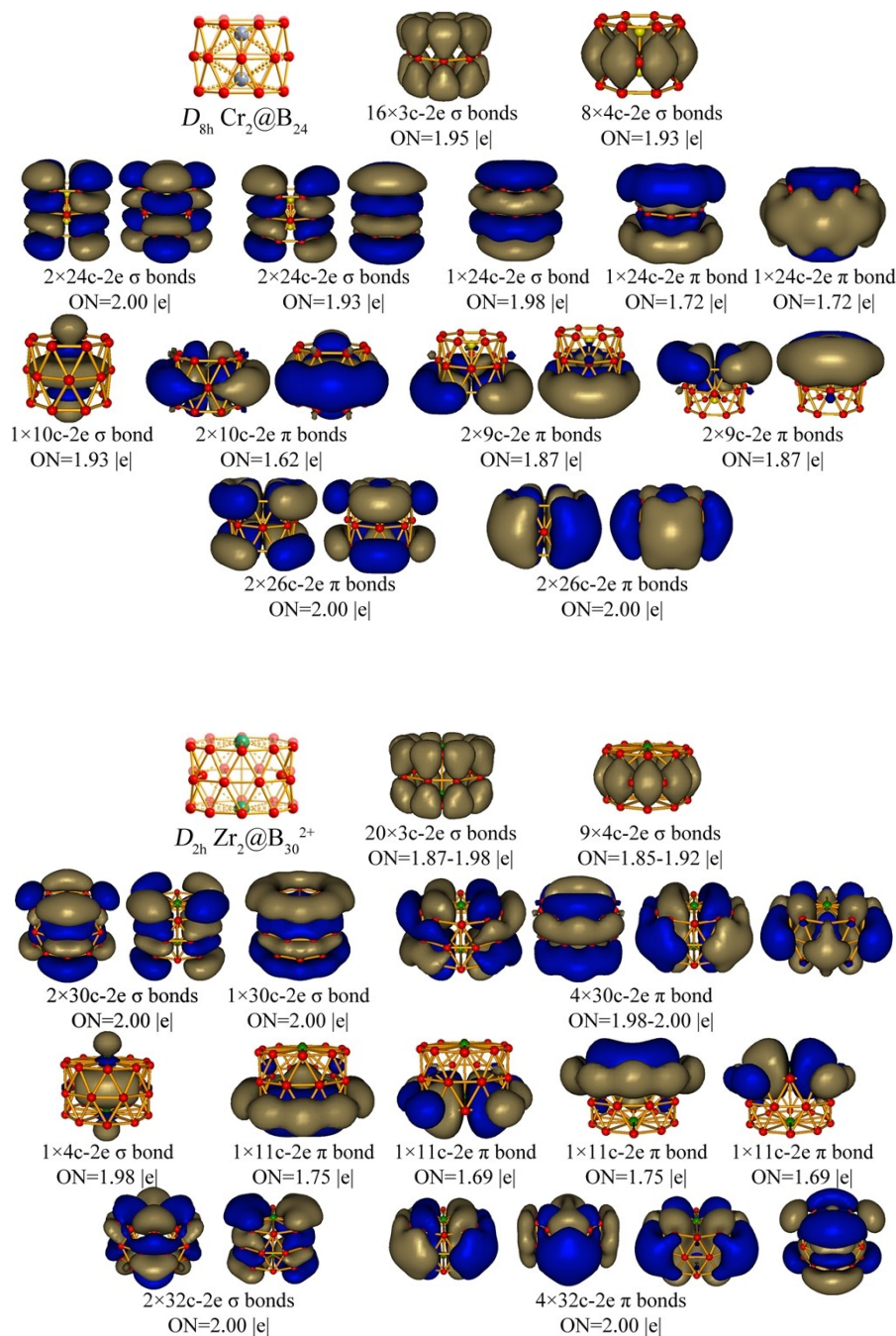
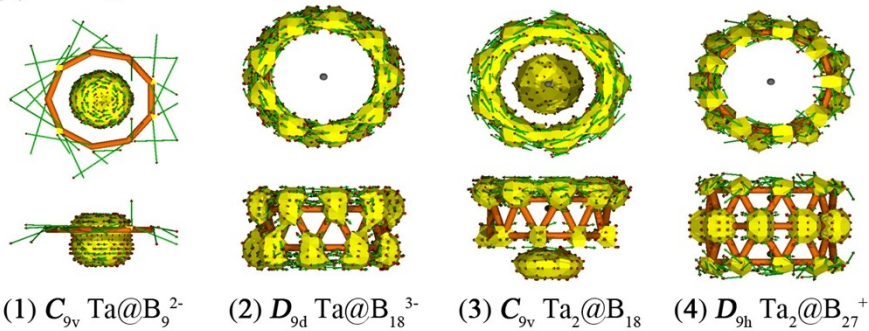
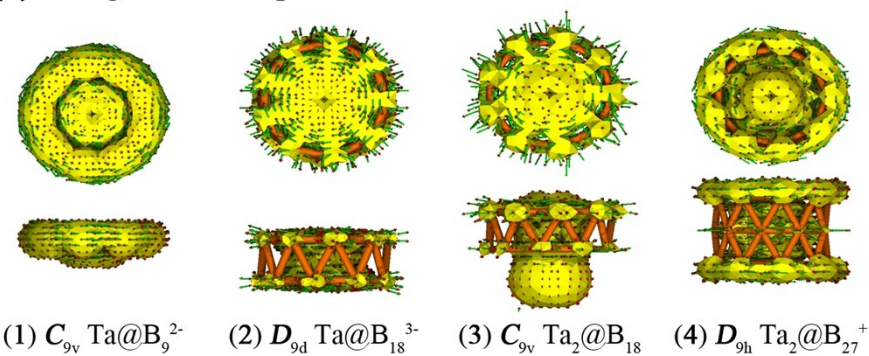


Figure S7 The top and side views of anisotropy of the current density (ACID) isosurfaces maps of **1-4** at an isosurface value of 0.05, Current density vectors are plotted onto the isosurface as arrows (green and red). The vector of the magnetic field is perpendicular to the diameter of tubes **1-4**.

(a) σ ring current maps



(b) π ring current maps



(c) $\sigma+\pi$ ring current maps

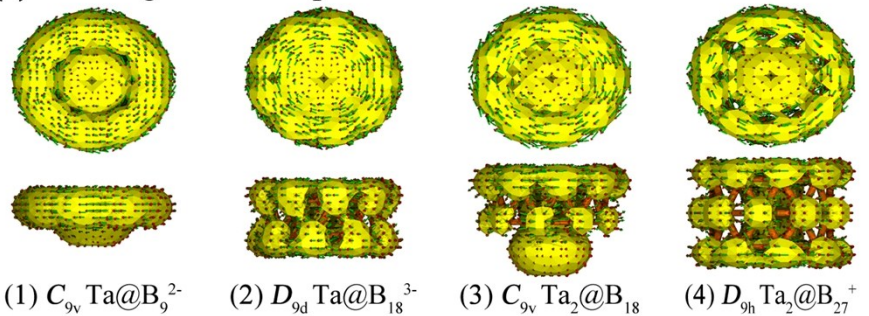


Figure S8 Comparison of the delocalized π -CMOs of bare D_{9h} B_{27}^+ ligand and D_{9h} $Ta_2@B_{27}^+(4)$ complex.

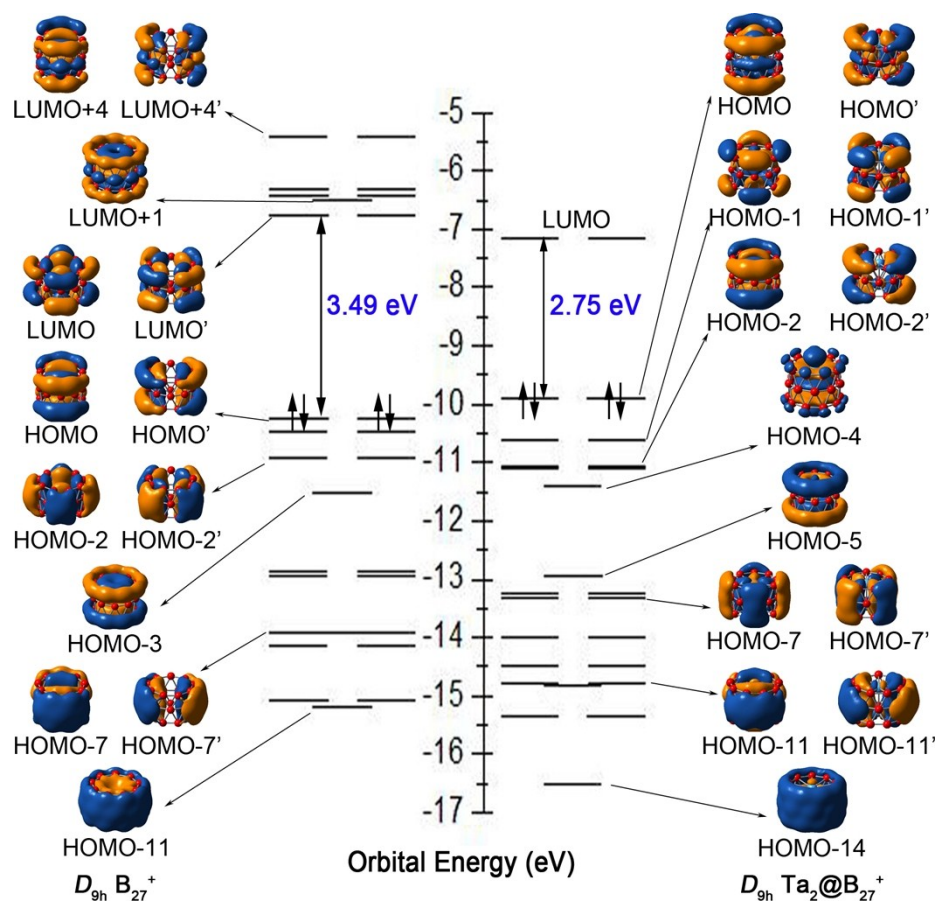


Table S1 Calculated Ta-Ta distances ($r_{\text{Ta-Ta}}/\text{\AA}$) and Wiberger bond indexes ($\text{WBI}_{\text{Ta-Ta}}$), Ta-B coordination distances ($r_{\text{Ta-B}}/\text{\AA}$) and bond orders ($\text{WBI}_{\text{Ta-B}}$), total bond orders (WBI_{Ta}), natural atomic charges ($q_{\text{Ta}}/|e|$), and electronic configurations of Ta centers, HOMO-LUMO energy gaps $\Delta E_{\text{gap}}/\text{eV}$, and the smallest vibrational frequencies $\nu_{\text{min}}/\text{cm}^{-1}$ of **1-4** at PBE0/6-311+G(d).

	$r_{\text{Ta-Ta}}/\text{\AA}$	$\text{WBI}_{\text{Ta-Ta}}$	$r_{\text{Ta-B}}/\text{\AA}$	$\text{WBI}_{\text{Ta-B}}$	WBI_{Ta}	q_{Ta}	e-Configurations	ΔE_{gap}	ν_{min}
C_{9v} Ta@B ₉ ²⁻ (1)			2.33	0.54	4.82	+0.75	Ta[Xe]5d ^{3.97} 6s ^{0.23}	2.28	111.06
D_{9d} Ta@B ₁₈ ³⁻ (2)	-	-	2.48	0.29	5.11	+0.50	Ta[Xe]5d ^{4.11} 6s ^{0.19}	0.82	130.50
C_{9v} Ta ₂ @B ₁₈ (3)	2.37	1.37	2.55	0.29	4.75	+0.92	Ta[Xe]5d ^{3.92} 6s ^{0.13}	2.93	171.60
			2.50	0.24	5.67	+0.42	Ta[Xe]5d ^{4.11} 6s ^{0.24}		
D_{9h} Ta ₂ @B ₂₇ ⁺ (4)	2.52	0.88	2.54	0.24	5.62	+0.34	Ta[Xe]5d ^{4.26} 6s ^{0.21}	2.75	194.10

Table S2 Optimized coordinates (x, y, z) of C_{9v} Ta@B₉²⁻(**1**), D_{9d} Ta@B₁₈³⁻(**2**), C_{9v} Ta₂@B₁₈(**3**), D_{9h} Ta₂@B₂₇⁺(**4**), D_{8h} Cr₂@B₂₄, and D_{2h} Zr₂@B₃₀²⁺ at PBE0/6-311+G(d) level.

(1) C_{9v} Ta@B₉²⁻

B	0.00000000	2.29024000	-0.27473400
B	-1.47213800	1.75442500	-0.27473400
B	2.25544600	0.39769600	-0.27473400
B	1.47213800	1.75442500	-0.27473400
B	0.78330800	-2.15212100	-0.27473400
B	1.98340600	-1.14512000	-0.27473400
B	-2.25544600	0.39769600	-0.27473400
B	-1.98340600	-1.14512000	-0.27473400
B	-0.78330800	-2.15212100	-0.27473400
Ta	0.00000000	0.00000000	0.16935700

(2) D_{9d} Ta@B₁₈³⁻

B	0.00000000	2.33299000	0.83549500
B	1.49961700	1.78717400	0.83549500
B	-2.29754700	0.40511900	0.83549500
B	-1.49961700	1.78717400	0.83549500
B	-0.79793000	-2.19229400	0.83549500
B	-2.02042900	-1.16649500	0.83549500
B	2.29754700	0.40511900	0.83549500
B	2.02042900	-1.16649500	0.83549500
B	0.79793000	-2.19229400	0.83549500
B	-2.29754700	-0.40511900	-0.83549500
B	-1.49961700	-1.78717400	-0.83549500
B	-0.79793000	2.19229400	-0.83549500
B	-2.02042900	1.16649500	-0.83549500
B	2.02042900	1.16649500	-0.83549500
B	0.79793000	2.19229400	-0.83549500
B	0.00000000	-2.33299000	-0.83549500
B	1.49961700	-1.78717400	-0.83549500
B	2.29754700	-0.40511900	-0.83549500
Ta	0.00000000	0.00000000	0.00000000

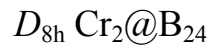
(3) C_{9v} Ta₂@B₁₈

B	0.00000000	2.27997900	0.34090600
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B	-2.24534100	0.39591400	0.34090600
B	-1.46554300	1.74656600	0.34090600
B	-0.77979900	-2.14248000	0.34090600
B	-1.97452000	-1.13999000	0.34090600
B	2.24534100	0.39591400	0.34090600
B	1.97452000	-1.13999000	0.34090600
B	0.77979900	-2.14248000	0.34090600
B	-2.33972700	-0.41255700	-1.30877900
B	-1.52714800	-1.81998500	-1.30877900
B	-0.81257900	2.23254200	-1.30877900
B	-2.05752200	1.18791100	-1.30877900
B	2.05752200	1.18791100	-1.30877900
B	0.81257900	2.23254200	-1.30877900
B	0.00000000	-2.37582100	-1.30877900
B	1.52714800	-1.81998500	-1.30877900
B	2.33972700	-0.41255700	-1.30877900
Ta	0.00000000	0.00000000	-0.88712500
Ta	0.00000000	0.00000000	1.48376000

(4) D_{9h} Ta₂@B₂₇⁺

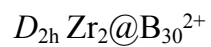
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B	-2.33672300	0.41202700	0.00000000
B	-2.05488000	-1.18638600	0.00000000
B	-0.81153500	-2.22967500	0.00000000
B	0.81153500	-2.22967500	0.00000000
B	2.05488000	-1.18638600	0.00000000
B	2.33672300	0.41202700	0.00000000
B	1.52518800	1.81764800	0.00000000
B	0.81162000	2.22990700	1.62638700
B	-0.81162000	2.22990700	1.62638700
B	-2.05509300	1.18650900	1.62638700
B	-2.33696600	-0.41207000	1.62638700
B	-1.52534600	-1.81783700	1.62638700
B	0.00000000	-2.37301800	1.62638700
B	1.52534600	-1.81783700	1.62638700
B	2.33696600	-0.41207000	1.62638700
B	2.05509300	1.18650900	1.62638700
B	-2.05509300	1.18650900	-1.62638700
B	-2.33696600	-0.41207000	-1.62638700
B	-1.52534600	-1.81783700	-1.62638700

B	0.00000000	-2.37301800	-1.62638700
B	1.52534600	-1.81783700	-1.62638700
B	2.33696600	-0.41207000	-1.62638700
B	2.05509300	1.18650900	-1.62638700
B	0.81162000	2.22990700	-1.62638700
B	-0.81162000	2.22990700	-1.62638700
Ta	0.00000000	0.00000000	1.25940000
Ta	0.00000000	0.00000000	-1.25940000



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B	-2.01605700	-0.83460200	0.00000000
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B	0.83460200	2.01605700	0.00000000
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B	1.49252300	-1.49252300	-1.57565500

B	2.11043800	0.00000000	-1.57681200
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Cr	0.00000000	0.00000000	1.04754400
Cr	0.00000000	0.00000000	-1.04754400



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B	2.12846400	1.51607100	-1.51995700
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Zr	0.00000000	0.00000000	-1.59496300