Electronic Supplementary Material (ESI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2021

Supporting Information

$TM_4B_{18}^{0/-}$ (TM = Hf, Ta, W, Re, Os): new structure construction with TM doped B wheel units

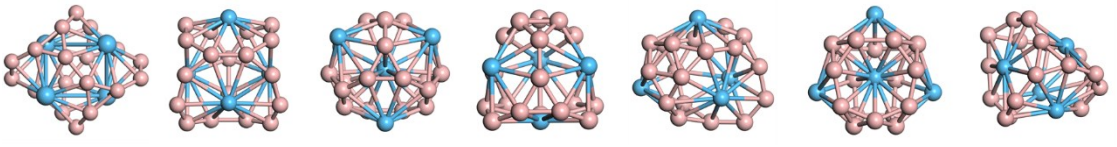
Zhen Wang, Qiuying Du, Sung Jin Park*

Key Laboratory of Materials Modification by Laser, Ion and Electron Beams (Dalian University of Technology), Ministry of Education, Dalian, 116024, China

* Corresponding author: *parksj@dlut.edu.cn*

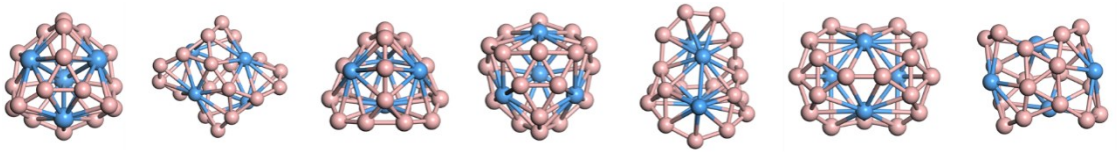
Fig. S1 Low-lying isomers of TM_4B_{18} (TM = Hf, Ta, W, Re, Os) at the levels of PBE0/TZVP.

Hf_4B_{18}



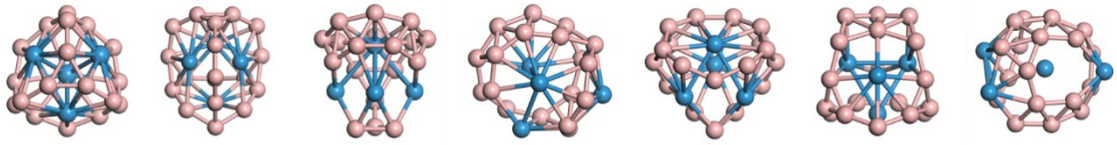
(D_2) (C_s) ΔE=0.782 eV (C_s) ΔE=1.079 eV (C_s) ΔE=1.210 eV (C_1) ΔE=1.236 eV (C_s) ΔE=1.590 eV (C_1) ΔE=2.639 eV

Ta_4B_{18}



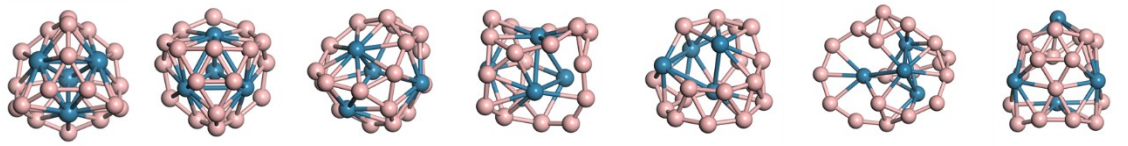
(T_d) (C_2) ΔE=1.114 eV (C_s) ΔE=1.374 eV (C_{3v}) ΔE=2.209 eV (C_1) ΔE=2.360 eV (C_{2v}) ΔE=2.622 eV (C_2) ΔE=2.821 eV

W_4B_{18}



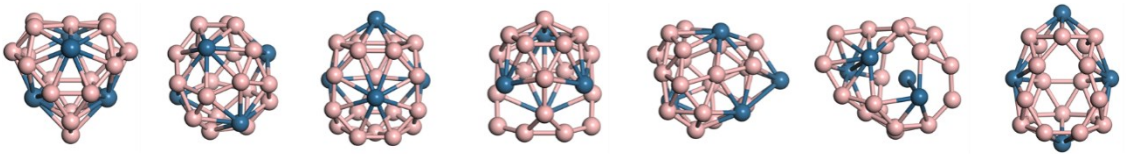
(C_{3v}) (C_s) ΔE=1.798 eV (C_s) ΔE=2.187 eV (C_1) ΔE=2.456 eV (C_s) ΔE=2.495 eV (C_s) ΔE=2.610 eV (C_1) ΔE=4.805 eV

Re_4B_{18}



(T_d) (C_s) ΔE=2.034 eV (C_1) ΔE=2.747 eV (C_1) ΔE=2.947 eV (C_1) ΔE=3.665 eV (C_1) ΔE=3.997 eV (C_1) ΔE=4.277 eV

Os_4B_{18}



(C_{2v}) (C_2) ΔE=0.124 eV (C_s) ΔE=0.504 eV (C_s) ΔE=0.778 eV (C_1) ΔE=1.259 eV (C_1) ΔE=1.344 eV (C_s) ΔE=1.360 eV

Table S1. The theoretical and experimental data for TM (TM = Hf, Ta, W, Re, Os) dimer: equilibrium bond lengths (R, in Å), vibrational frequencies (ω, in cm^{-1}), and magnetic moments (μ, in μ_B). The values were calculated by using PBE0 functional under the basis set of def2-TZVP or LanL2DZ.

	def2-TZVP			LanL2DZ			Experiment		
	R (Å)	ω (cm^{-1})	μ	R (Å)	ω (cm^{-1})	μ	R (Å)	ω (cm^{-1})	μ
Hf_2	2.40	229.9	2	2.61	193.4	2	2.46	176.2±2.6	2^1
Ta_2	2.23	284.3	4	2.25	295.3	4	2.23	300.2±1.2	4^1
W_2	2.00	421.0	0	2.02	423.8	0	2.18	336.8	0^1
Re_2	2.01	411.84	2	2.04	407.5	2	2.18	340±20	2^1
Os_2	2.22	302.3	6	2.36	266.0	6	*2.2±0.05*	*300±20*	*4/6*[2, 3]

References

(1) X. Sun, J. Du, P. Zhang and G. Jiang, *J. Clust. Sci.*, 2010, **21**, 619-636.

(2) J. Du, X. Sun and H. Wang, *Int. J. Quantum Chem.*, 2008, **108**, 1505-1517.

(3) J. Kim and J. Kim, *Int. J. Quantum Chem.*, 2014, **114**, 1466-1471.

Table S2. The coordinates of the lowest energy structures of TM_4B_{18} (TM = Hf, Ta, W, Re, Os) at the levels of PBE0/TZVP.

Hf_4B_{18}

B	0.70651100	1.20388200	2.15974200
B	-0.70651100	-1.20388200	2.15974200
B	0.00000000	0.00000000	2.88498400
B	-0.70651100	1.20388200	-2.15974200
B	-2.07058300	1.45831100	-1.04040900
B	-0.54728100	1.83538900	-0.64737800
B	-3.26659100	0.63343900	-0.43182200
B	-3.26659100	-0.63343900	0.43182200
B	-2.07058300	-1.45831100	1.04040900
B	0.54728100	1.83538900	0.64737800
B	-0.54728100	-1.83538900	0.64737800
B	2.07058300	-1.45831100	-1.04040900
B	0.54728100	-1.83538900	-0.64737800
B	2.07058300	1.45831100	1.04040900
B	3.26659100	-0.63343900	-0.43182200
B	0.00000000	0.00000000	-2.88498400
B	0.70651100	-1.20388200	-2.15974200
B	3.26659100	0.63343900	0.43182200
Hf	-1.54379500	0.88594600	1.29151100
Hf	-1.54379500	-0.88594600	-1.29151100
Hf	1.54379500	-0.88594600	1.29151100
Hf	1.54379500	0.88594600	-1.29151100

Ta_4B_{18}

B	-0.99553200	0.99553200	2.19516900
B	0.00000000	0.00000000	2.87894200
B	0.99553200	-0.99553200	2.19516900
B	-2.19516900	0.99553200	0.99553200
B	-0.99553200	2.19516900	0.99553200
B	0.00000000	2.87894200	0.00000000
B	0.99553200	2.19516900	-0.99553200
B	2.87894200	0.00000000	0.00000000
B	2.19516900	-0.99553200	0.99553200
B	0.99553200	-2.19516900	0.99553200
B	2.19516900	0.99553200	-0.99553200
B	0.00000000	-2.87894200	0.00000000
B	-0.99553200	-2.19516900	-0.99553200

B	-2.19516900	-0.99553200	-0.99553200
B	-2.87894200	0.00000000	0.00000000
B	0.99553200	0.99553200	-2.19516900
B	0.00000000	0.00000000	-2.87894200
B	-0.99553200	-0.99553200	-2.19516900
Ta	1.06468000	1.06468000	1.06468000
Ta	-1.06468000	-1.06468000	1.06468000
Ta	1.06468000	-1.06468000	-1.06468000
Ta	-1.06468000	1.06468000	-1.06468000

W_4B_{18}

B	-2.03353300	1.17406100	1.70242400
B	0.00000000	0.97512100	-2.28906400
B	0.84447900	-0.48756000	-2.28906400
B	-0.84447900	-0.48756000	-2.28906400
B	0.00000000	2.35600200	-1.56586400
B	0.00000000	2.64042900	-0.03680600
B	0.85986300	2.14523400	1.32222400
B	-0.85986300	2.14523400	1.32222400
B	0.00000000	-2.34812200	1.70242400
B	-2.28775900	-0.32795400	1.32222400
B	-1.42789600	-1.81728100	1.32222400
B	-2.04035700	-1.17800100	-1.56586400
B	2.04035700	-1.17800100	-1.56586400
B	2.28667900	-1.32021500	-0.03680600
B	2.03353300	1.17406100	1.70242400
B	2.28775900	-0.32795400	1.32222400
B	1.42789600	-1.81728100	1.32222400
B	-2.28667900	-1.32021500	-0.03680600
W	1.45615100	0.84070900	-0.52171300
W	-1.45615100	0.84070900	-0.52171300
W	0.00000000	-1.68141900	-0.52171300
W	0.00000000	0.00000000	1.47288000

Re_4B_{18}

B	2.25714400	0.84714300	0.99451000
B	-1.40776800	0.00000000	2.19469600
B	1.40776800	0.00000000	2.19469600
B	0.00000000	0.00000000	2.88515700
B	2.04035900	2.04035900	0.00000000

B	0.84714300	2.25714400	-0.99451000
B	-0.84714300	2.25714400	-0.99451000
B	-2.04035900	2.04035900	0.00000000
B	-2.25714400	-0.84714300	0.99451000
B	-2.25714400	0.84714300	0.99451000
B	2.25714400	-0.84714300	0.99451000
B	2.04035900	-2.04035900	0.00000000
B	0.84714300	-2.25714400	-0.99451000
B	0.00000000	1.40776800	-2.19469600
B	-0.84714300	-2.25714400	-0.99451000
B	-2.04035900	-2.04035900	0.00000000
B	0.00000000	0.00000000	-2.88515700
B	0.00000000	-1.40776800	-2.19469600
Re	0.00000000	1.28567000	0.91125400
Re	0.00000000	-1.28567000	0.91125400
Re	1.28567000	0.00000000	-0.91125400
Re	-1.28567000	0.00000000	-0.91125400

Os_4B_{18}

B	0.00000000	2.49075300	-0.74035200
B	2.02520200	0.85442100	0.78268500
B	1.36159800	0.00000000	2.08315200
B	1.46231700	1.87839700	-0.34880900
B	-1.46231700	1.87839700	-0.34880900
B	-1.36159800	0.00000000	2.08315200
B	-2.02520200	0.85442100	0.78268500
B	0.82805700	1.55985500	-1.91185000
B	2.02520200	-0.85442100	0.78268500
B	1.46231700	-1.87839700	-0.34880900
B	0.00000000	0.00000000	2.85330600
B	0.82805700	-1.55985500	-1.91185000
B	-0.82805700	1.55985500	-1.91185000
B	0.00000000	0.00000000	-1.90524400
B	-1.46231700	-1.87839700	-0.34880900
B	-0.82805700	-1.55985500	-1.91185000
B	-2.02520200	-0.85442100	0.78268500
B	0.00000000	-2.49075300	-0.74035200
Os	0.00000000	1.57030000	1.24152500
Os	0.00000000	-1.57030000	1.24152500
Os	2.02770400	0.00000000	-1.16658300
Os	-2.02770400	0.00000000	-1.16658300

Table S3. The coordinates of the lowest energy structures of $TM_4B_{18}^-$ (TM = Hf, Ta, W, Re, Os) at the levels of PBE0/TZVP.

$Hf_4B_{18}^-$

B	-0.70118400	2.11963000	1.22842100
B	0.70118400	2.14303400	-1.19767300
B	0.00490700	2.86004300	0.01857400
B	0.70118400	-2.11963000	1.22842100
B	2.03961300	-1.04970800	1.47010600
B	0.53342100	-0.65476900	2.03259800
B	3.25088000	-0.44725500	0.64703900
B	3.25979400	0.42096300	-0.62163900
B	2.07162400	1.02137900	-1.47283100
B	-0.53342100	0.65476900	2.03259800
B	0.54895800	0.64710900	-1.87842700
B	-2.07162400	-1.02137900	-1.47283100
B	-0.54895800	-0.64710900	-1.87842700
B	-2.03961300	1.04970800	1.47010600
B	-3.25979400	-0.42096300	-0.62163900
B	-0.00490700	-2.86004300	0.01857400
B	-0.70118400	-2.14303400	-1.19767300
B	-3.25088000	0.44725500	0.64703900
Hf	1.48794000	1.22124800	0.89906300
Hf	1.55209300	-1.29877800	-0.91477000
Hf	-1.55209300	1.29877800	-0.91477000
Hf	-1.48794000	-1.22124800	0.89906300

$Ta_4B_{18}^-$

B	0.00000000	2.59065100	-0.14163000
B	0.00000000	2.34389700	-1.69702800
B	0.00000000	0.98041700	-2.48024400
B	0.84607100	2.10996100	1.25356400
B	-0.84607100	2.10996100	1.25356400
B	-2.25031500	-0.32226100	1.25356400
B	-2.04453200	1.18041100	1.64148900
B	-2.02987400	-1.17194900	-1.69702800
B	-0.84906600	-0.49020900	-2.48024400
B	0.84906600	-0.49020900	-2.48024400

B	-2.24357000	-1.29532600	-0.14163000
B	2.02987400	-1.17194900	-1.69702800
B	2.24357000	-1.29532600	-0.14163000
B	2.25031500	-0.32226100	1.25356400
B	2.04453200	1.18041100	1.64148900
B	-1.40424400	-1.78769900	1.25356400
B	1.40424400	-1.78769900	1.25356400
B	0.00000000	-2.36082200	1.64148900
Ta	-1.47311800	0.85050500	-0.63097500
Ta	1.47311800	0.85050500	-0.63097500
Ta	0.00000000	-1.70101000	-0.63097500
Ta	0.00000000	0.00000000	1.92791500

$W_4B_{18}^-$

B	-2.02951400	-1.17174000	-1.60915000
B	0.00000000	2.62758500	-0.07278700
B	0.85283400	2.14140900	1.29798700
B	-0.85283400	2.14140900	1.29798700
B	0.00000000	2.34348100	-1.60915000
B	0.00000000	0.97456000	-2.36318800
B	0.84399400	-0.48728000	-2.36318800
B	-0.84399400	-0.48728000	-2.36318800
B	0.00000000	-2.34955000	1.67180900
B	-2.27555500	-1.31379300	-0.07278700
B	-1.42809700	-1.80928000	1.29798700
B	-2.03477000	1.17477500	1.67180900
B	2.03477000	1.17477500	1.67180900
B	2.28093100	-0.33212800	1.29798700
B	2.02951400	-1.17174000	-1.60915000
B	2.27555500	-1.31379300	-0.07278700
B	1.42809700	-1.80928000	1.29798700
B	-2.28093100	-0.33212800	1.29798700
W	1.41551100	0.81724600	-0.53770900
W	-1.41551100	0.81724600	-0.53770900
W	0.00000000	0.00000000	1.56799400
W	0.00000000	-1.63449200	-0.53770900

$Re_4B_{18}^-$

B	2.24774700	0.84764800	1.00771800
B	-1.40238800	0.00000000	2.23189300
B	1.40238800	0.00000000	2.23189300
B	0.00000000	0.00000000	2.93860200
B	2.03528000	2.03528000	0.00000000
B	0.84764800	2.24774700	-1.00771800
B	-0.84764800	2.24774700	-1.00771800
B	-2.03528000	2.03528000	0.00000000
B	-2.24774700	-0.84764800	1.00771800
B	-2.24774700	0.84764800	1.00771800
B	2.24774700	-0.84764800	1.00771800
B	2.03528000	-2.03528000	0.00000000
B	0.84764800	-2.24774700	-1.00771800
B	0.00000000	1.40238800	-2.23189300
B	-0.84764800	-2.24774700	-1.00771800
B	-2.03528000	-2.03528000	0.00000000
B	0.00000000	0.00000000	-2.93860200
B	0.00000000	-1.40238800	-2.23189300
Re	0.00000000	1.27046000	0.91277800
Re	0.00000000	-1.27046000	0.91277800
Re	1.27046000	0.00000000	-0.91277800
Re	-1.27046000	0.00000000	-0.91277800

$Os_4B_{18}^-$

B	0.00000000	2.47429100	-0.72918800
B	2.03098300	0.85228100	0.79900600
B	1.36568100	0.00000000	2.12381600
B	1.45875100	1.85495000	-0.34835800
B	-1.45875100	1.85495000	-0.34835800
B	-1.36568100	0.00000000	2.12381600
B	-2.03098300	0.85228100	0.79900600
B	0.82430300	1.55310300	-1.93353800
B	2.03098300	-0.85228100	0.79900600
B	1.45875100	-1.85495000	-0.34835800
B	0.00000000	0.00000000	2.91095500
B	0.82430300	-1.55310300	-1.93353800
B	-0.82430300	1.55310300	-1.93353800
B	0.00000000	0.00000000	-1.88029200
B	-1.45875100	-1.85495000	-0.34835800
B	-0.82430300	-1.55310300	-1.93353800
B	-2.03098300	-0.85228100	0.79900600

B	0.00000000	-2.47429100	-0.72918800
Os	0.00000000	1.53415400	1.22708700
Os	0.00000000	-1.53415400	1.22708700
Os	2.04997700	0.00000000	-1.15762500
Os	-2.04997700	0.00000000	-1.15762500