Supplementary Materials

Pentacoordinated pyramidal structures and bonding properties of $WN_{10}^{-/0}$: anion photoelectron spectroscopy and theoretical calculations

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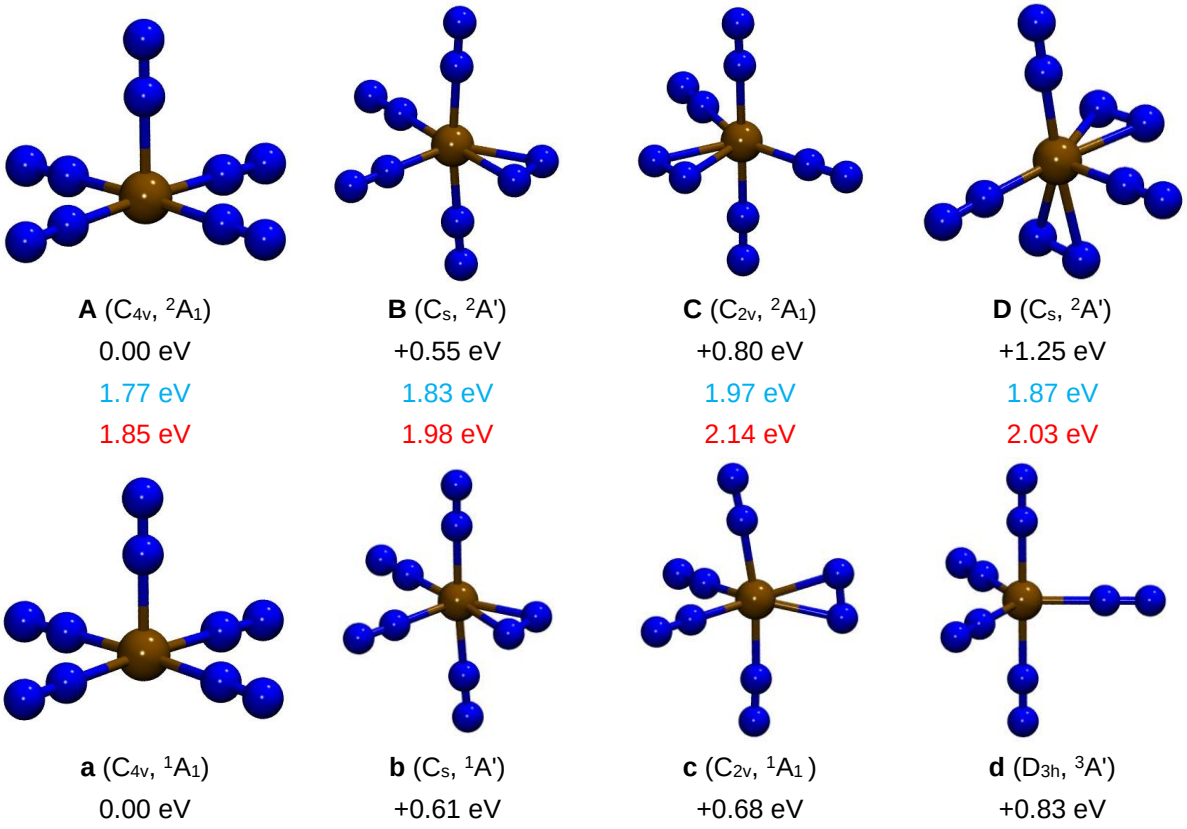


Fig. S1 Typical low-lying isomers of $WN_{10}^{-/0}$ clusters optimized at the B3LYP-D3BJ/ma-TZVP. The relative energies were calculated at the same level. The brown/blue balls stand for W/N, respectively. The value in blue/red value stand ADE/VDE of corresponding cluster.

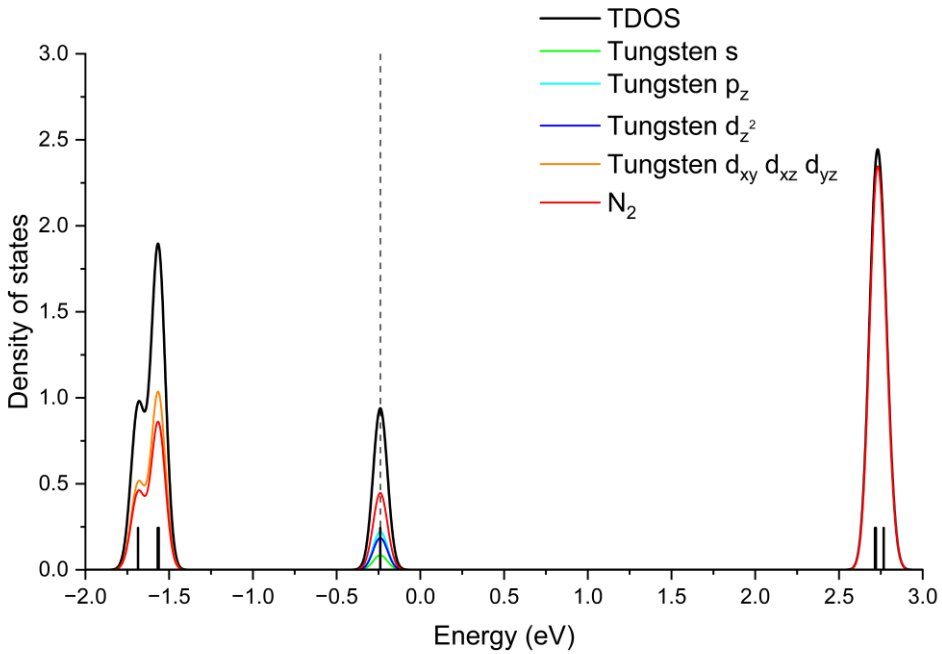


Fig. S2 DOS map of the WN_{10}^-. The dashed line represents the location of the HOMO.

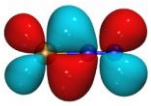
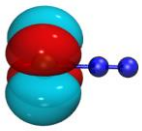
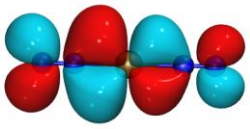
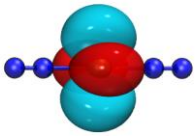
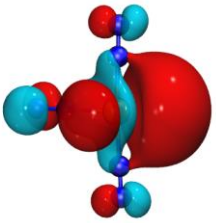
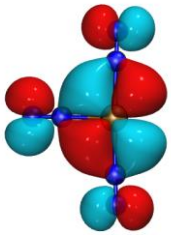
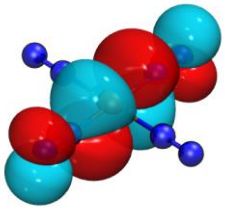
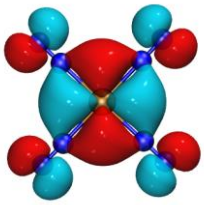
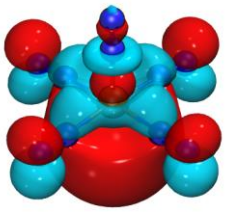
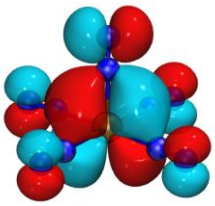
WN_2^-		WN_2^+	
WN_4^-		WN_4^+	
WN_6^-		WN_6^+	
WN_8^-		WN_8^+	
WN_{10}^-		WN_{10}^+	

Fig. S3 HOMOs of $W(N_2)_n^{-/0}$ (n=1-5) at the PBE0/ma-TZVP level. Isosurface value is 0.02.

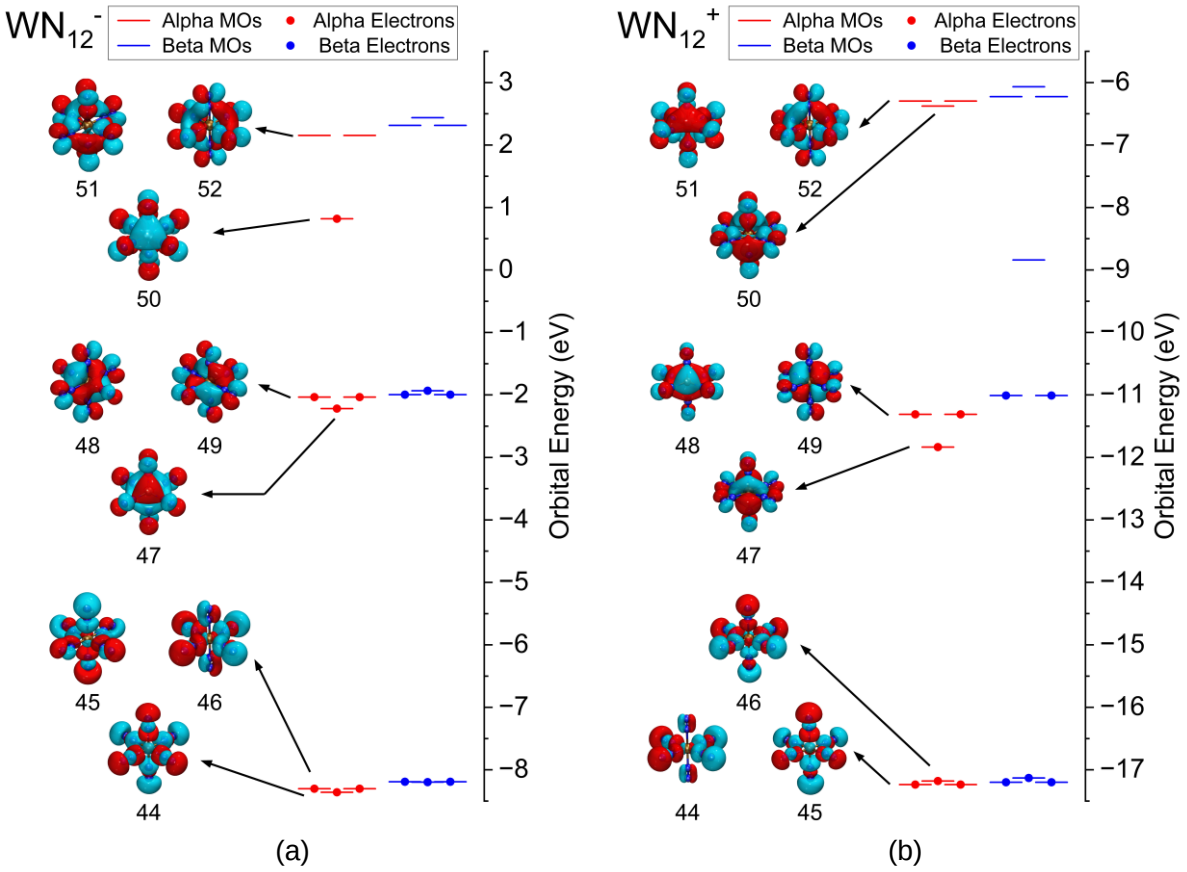


Fig. S4 Energy levels and diagrams of the molecular orbitals of the $WN_{12}^{-/+}$ at the PBE0/ma-TZVP level. Isosurface value is 0.02.

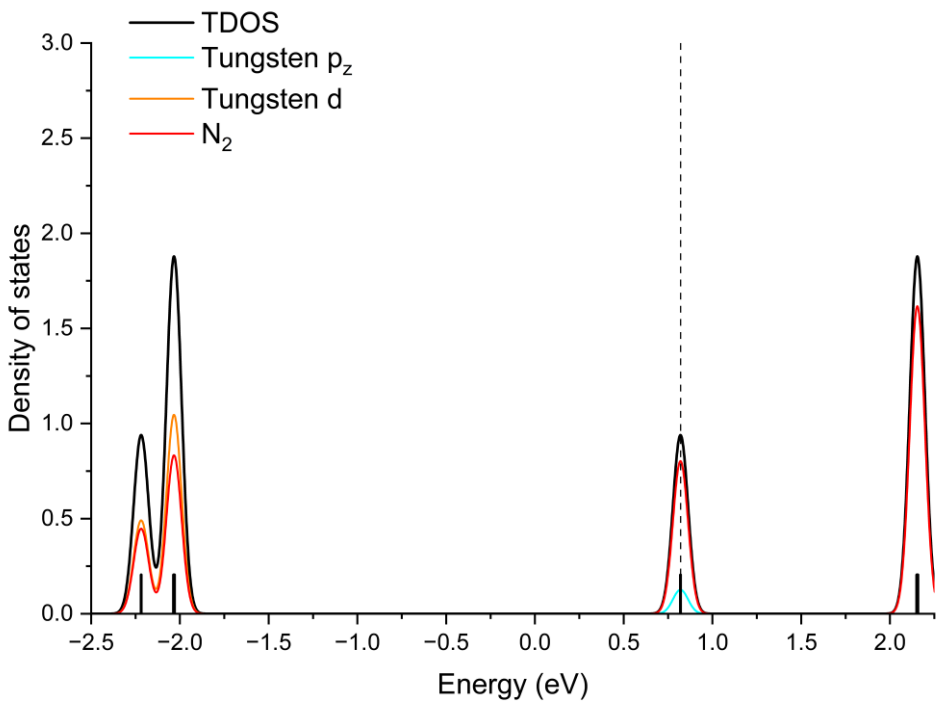


Fig. S5 DOS map of the WN_{12}^-. The dashed line represents the location of the HOMO.

Table S1 The experimental VDEs of WN_{10}^- compared with computational values using the TD-PBE0 method

	VDE (eV) (Expt.)	VDE (eV) (Comput.)[a]	Final state	Final electronic configuration[c]
	1.582	1.507[b]	$^1A_1$	$2B_1^2 19E^2 20E^2 \mathbf{14A_1^0}$
A	2.53	2.46	^3E	$2B_1^2 \mathbf{19E^1} 20E^2 14A_1^1$
B	2.58	2.46	^3E	$2B_1^2 19E^2 \mathbf{20E^1} 14A_1^1$
C	2.62			
D	2.75	2.88	$^3B_1$	$\mathbf{2B_1^1} 19E^2 20E^2 14A_1^1$
E	2.80			
F	2.83			
G	2.99	3.16	$^1B_1$	$\mathbf{2B_1^1} 19E^2 20E^2 14A_1^1$
H	3.03			
I	3.08			
J	3.13	3.21	^1E	$2B_1^2 19E^2 \mathbf{20E^1} 14A_1^1$
K	3.17	3.21	^1E	$2B_1^2 \mathbf{19E^1} 20E^2 14A_1^1$
L	3.22			
M	3.25			
N	3.28			
O	3.33			
P	3.38			

[a] The excited states of the one-electron-detached species were obtained from TDDFT calculations of the neutrals.

[b] The first VDE was obtained by the CCSD(T) method.

[c] The orbitals labeled in bold are the major electron detachment channels.

Table S2 T1 diagnostic factors of $WN_{10}^{-/0}$ clusters

	WN_{10}^{-}				WN_{10}			
Isomers	10A	10B	10C	10D	10a	10b	10c	10d
T1	0.036	0.033	0.036	0.037	0.017	0.015	0.015	0.025

Table S3 Cartesian atomic coordinates of the typical low-lying isomers of WN_{10}^- optimized with PBE0 functional

10A

W	0.00000000	0.00000000	0.17064900
N	0.00000000	2.00596300	0.31834800
N	-2.00596300	0.00000000	0.31834800
N	0.00000000	0.00000000	-1.78911700
N	2.00596300	0.00000000	0.31834800
N	0.00000000	-2.00596300	0.31834800
N	0.00000000	-3.12457300	0.40641700
N	0.00000000	3.12457300	0.40641700
N	0.00000000	0.00000000	-2.91394400
N	3.12457300	0.00000000	0.40641700
N	-3.12457300	0.00000000	0.40641700

10B

W	-0.00189100	-0.16403800	0.00000000
N	-0.00003300	-0.27835300	2.00269300
N	-2.23246300	-0.50339400	0.00000000
N	-0.00003300	-0.27835300	-2.00269300
N	-0.40742500	1.76833600	0.00000000
N	1.95642300	0.11719600	0.00000000
N	3.07035200	0.29469300	0.00000000
N	-0.00003300	-0.35424700	3.12128200
N	-0.00003300	-0.35424700	-3.12128200
N	-0.64206700	2.86394900	0.00000000
N	-1.72470300	-1.54146100	0.00000000

10C

W	0.00000000	0.00000000	0.10495500
N	0.00000000	1.97072100	0.53403200
N	-1.99856400	0.00000000	0.09371600
N	0.00000000	-1.97072100	0.53403200
N	0.00000000	-0.57544800	-2.04940900 N
1.99856400	0.00000000	0.09371600	
N	3.12069100	0.00000000	0.06297700
N	0.00000000	3.05889800	0.80392400
N	0.00000000	-3.05889800	0.80392400
N	0.00000000	0.57544800	-2.04940900
N	-3.12069100	0.00000000	0.06297700

10D

W	0.15851000	0.02995400	0.00000000
N	1.15983900	1.41827700	1.42974500
N	0.05596500	1.72317000	1.51172800
N	1.15983900	1.41827700	-1.42974500
N	0.05596500	1.72317000	-1.51172800
N	0.16453700	-1.34479000	-1.40184000
N	0.16453700	-2.12002500	-2.22184200
N	-1.82519200	0.13455400	0.00000000
N	-2.94024000	0.19552500	0.00000000
N	0.16453700	-1.34479000	1.40184000
N	0.16453700	-2.12002500	2.22184200

Table S4 Cartesian atomic coordinates of the typical low-lying isomers of WN_{10} optimized with PBE0 functional

10a

W	0.00000000	0.00000000	0.21690700
N	0.00000000	2.02678600	0.26647000
N	2.02678600	0.00000000	0.26647000
N	0.00000000	-2.02678600	0.26647000
N	-2.02678600	0.00000000	0.26647000
N	0.00000000	0.00000000	-1.73186800
N	0.00000000	0.00000000	-2.84651700
N	0.00000000	3.13617400	0.30487200
N	0.00000000	-3.13617400	0.30487200
N	-3.13617400	0.00000000	0.30487200
N	3.13617400	0.00000000	0.30487200

10b

W	0.13636200	-0.15983600	0.00000000
N	0.13705100	-0.21243500	2.02278100
N	-1.58584500	-1.67736200	0.00000000
N	0.13705100	-0.21243500	-2.02278100
N	-1.34293700	1.13926700	0.00000000
N	1.46395700	1.33315500	0.00000000
N	2.22476200	2.14528200	0.00000000
N	0.13705100	-0.24913200	3.13224400
N	0.13705100	-0.24913200	-3.13224400
N	-2.16299800	1.88818200	0.00000000
N	-0.58668700	-2.21569800	0.00000000

10c

W	-0.06130300	0.18576300	0.00000000
N	-0.06856200	-0.11228900	3.14265900
N	-0.06856200	0.02548700	2.04720400
N	-0.06856200	0.02548700	-2.04720400
N	-0.06856200	-0.11228900	-3.14265900
N	-0.00470800	2.26973100	0.57677500
N	-0.00470800	2.26973100	-0.57677500
N	1.52799300	-0.96587400	0.00000000
N	2.46725000	-1.56762800	0.00000000
N	-1.18981900	-1.45890000	0.00000000
N	-1.87370400	-2.33723600	0.00000000

10d

W	0.00000000	0.00000000	0.00000000
N	0.00000000	2.01650100	0.00000000
N	0.00000000	0.00000000	2.03259700
N	-1.74634100	-1.00825000	0.00000000
N	0.00000000	0.00000000	-2.03259700
N	1.74634100	-1.00825000	0.00000000
N	2.71252800	-1.56607900	0.00000000
N	0.00000000	3.13215700	0.00000000
N	-2.71252800	-1.56607900	0.00000000
N	0.00000000	0.00000000	-3.14072500
N	0.00000000	0.00000000	3.14072500