Electronic Supplementary Information

Polymeric tungsten carbide nanoclusters: structural evolution, ligand modulation, and assembled nanomaterials

Jun Li,[a] Hai-Cai Huang,[a] Jing Wang,[a] Yang Zhao,[a] Jing Chen,[ab] Yu-Xiang Bu[ac] and Shi-Bo Cheng*[a]

[a]*Key Laboratory for Colloid and Interface Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, People's Republic of China*

[b]*Suzhou Institute of Shandong University, Suzhou, Jiangsu 215123, People's Republic of China*

[c]*School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, People's Republic of China*

Table S1 Theoretical structural and energetic parameters of WC and WC^- calculated at different functionals and basis sets. The available experimental values are included for comparison. The bond length and VDE are represented by r_e (in Å) and VDE (in eV), respectively.

		theor.			exp.		
		WC	WC^-		WC	WC^-	
functionals	basis sets	r_e	r_e	VDE	r_e	r_e	VDE
B3LYP	Genecp[d]	1.70	1.72	2.05	1.71[a]	1.77[b]	2.14[c]
	def2-TZVPP	1.70	1.72	1.92			
	Genecp[e]	1.70	1.73	1.98			
PBE0	Genecp[d]	1.69	1.71	1.81			
	def2-TZVPP	1.70	1.71	1.70			
	Genecp[e]	1.70	1.72	1.76			
M06-2X	Genecp[d]	1.67	1.70	1.71			
	def2-TZVPP	1.68	1.70	1.61			
	Genecp[e]	1.68	1.70	1.64			
B3PW91	Genecp[d]	1.70	1.72	1.86			
	def2-TZVPP	1.70	1.72	1.75			
	Genecp[e]	1.71	1.72	1.83			

[a]Experimental data extracted from *J. Chem. Phys.*, **2002**, 116, 993.

[b]Experimental data extracted from *J. Chem. Phys.*, **2008**, 129, 114304.

[c]Experimental data extracted from *Proc. Natl. Acad. Sci. U.S.A.,* **2010**, 107, 975.

[d]Genecp (LANL2TZ for W and aug-cc-PVTZ for C)

[e]Genecp (LANL08 for W and 6-311G* for C)

Table S2 Theoretical fragmentation energies (E_f, in eV) of W_2C_2 and W_3C_3 for distinct dissociation channels.

Dissociation channels	E_f/eV	Dissociation channels	E_f/eV
$W_2C_2 \rightarrow WC + WC$	6.84	$W_3C_3 \rightarrow W_2 + WC_3$	7.07
$W_2C_2 \rightarrow W_2 + C_2$	8.30	$W_3C_3 \rightarrow W_3 + C_3$	7.09
$W_2C_2 \rightarrow W + WC_2$	8.36	$W_3C_3 \rightarrow W_2C + WC_2$	6.69
$W_2C_2 \rightarrow C + W_2C$	8.80	$W_3C_3 \rightarrow W_2C_3 + W$	8.39
		$W_3C_3 \rightarrow W_3C_2 + C$	8.54
		$W_3C_3 \rightarrow W_2C_2 + WC$	6.17
		$W_3C_3 \rightarrow C_2 + W_3C$	7.50

Table S3 Theoretical fragmentation energies (E_f, in eV) of $(WC)_n$ (n = 2-7) for distinct fragmentation channels.

Dissociation channels	E_f/eV	Dissociation channels	E_f/eV
$W_2C_2 \rightarrow WC + WC$	6.84	$W_6C_6 \rightarrow W_5C_5 + WC$	8.20
$W_3C_3 \rightarrow W_2C_2 + WC$	6.17	$W_6C_6 \rightarrow W_4C_4 + W_2C_2$	7.79
$W_4C_4 \rightarrow W_3C_3 + WC$	7.42	$W_6C_6 \rightarrow W_3C_3 + W_3C_3$	9.04
$W_4C_4 \rightarrow W_2C_2 + W_2C_2$	6.76	$W_7C_7 \rightarrow W_6C_6 + WC$	6.60
$W_5C_5 \rightarrow W_4C_4 + WC$	6.43	$W_7C_7 \rightarrow W_5C_5 + W_2C_2$	7.96
$W_5C_5 \rightarrow W_3C_3 + W_2C_2$	7.01	$W_7C_7 \rightarrow W_4C_4 + W_3C_3$	8.21

Table S4 Becke population analysis for the spin magnetic moments of the total W, C, CO and PH_3 in $W_4C_4L_n$ (L = CO, PH_3; n = 0-6).

		local magnetic moment (μB)						
		0	1	2	3	4	5	6
$W_4C_4(CO)_n$	W	2.05	3.64	3.27	2.03	4.63	2.95	2.98
	C	-0.05	-0.15	-0.12	-0.23	-0.23	-0.19	-0.18
	CO	-	0.51	0.86	0.20	1.61	1.24	1.20
$W_4C_4(PH_3)_n$	W	2.05	3.93	2.01	3.45	3.35	3.24	3.43
	C	-0.05	-0.08	-0.08	-0.13	-0.16	-0.14	-0.19
	PH_3	-	0.16	0.08	0.68	0.81	0.90	0.76

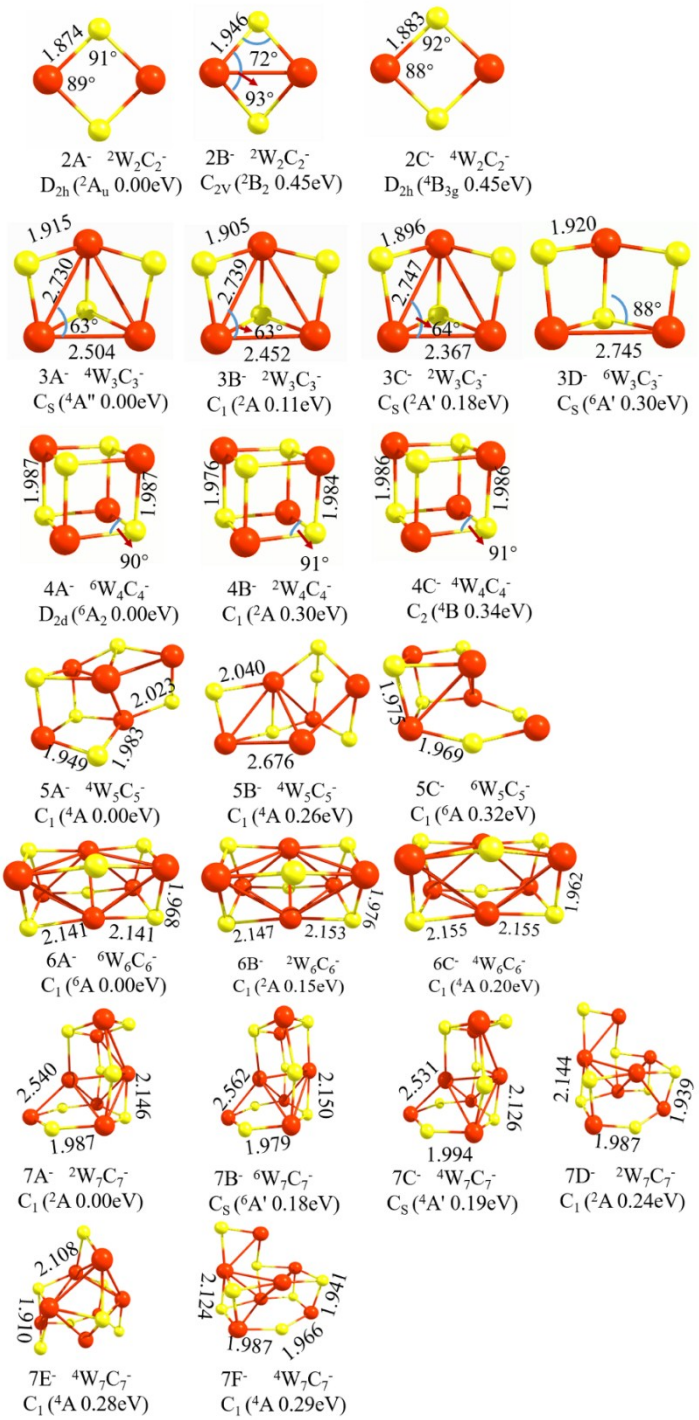

Fig. S1 Theoretical global minima and selected lower-lying isomers of the anionic $(WC)_n$ (n = 2-7) clusters. The total energies of isomers are given with respect to the energies of the global minima of the corresponding clusters.

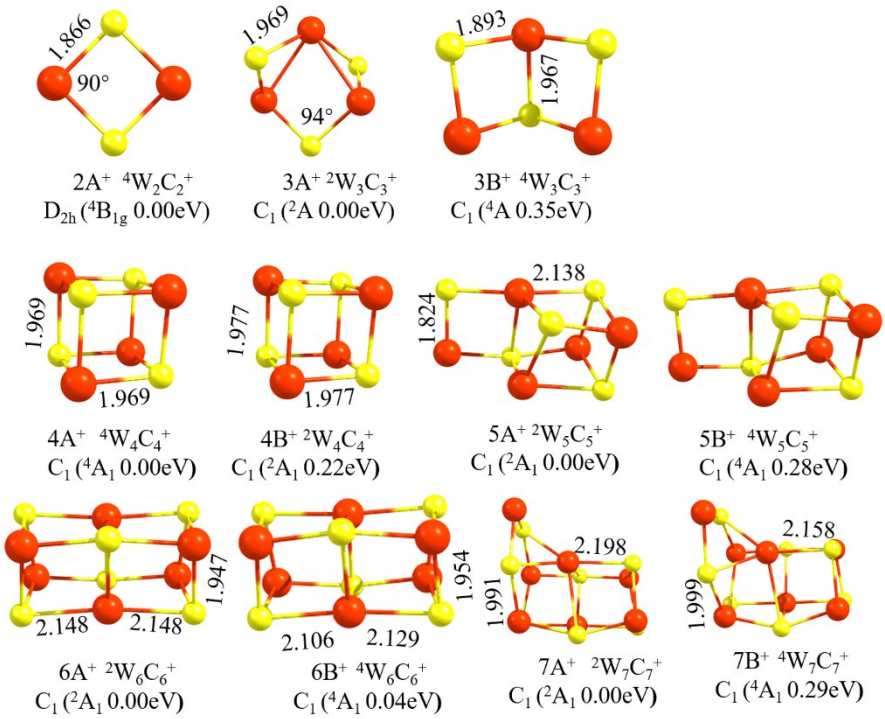

Fig. S2 Theoretical global minima and selected lower-lying isomers of the cationic $(WC)_n$ (n = 2-7) clusters. The total energies of isomers are given with respect to the energies of the global minima of the corresponding clusters.

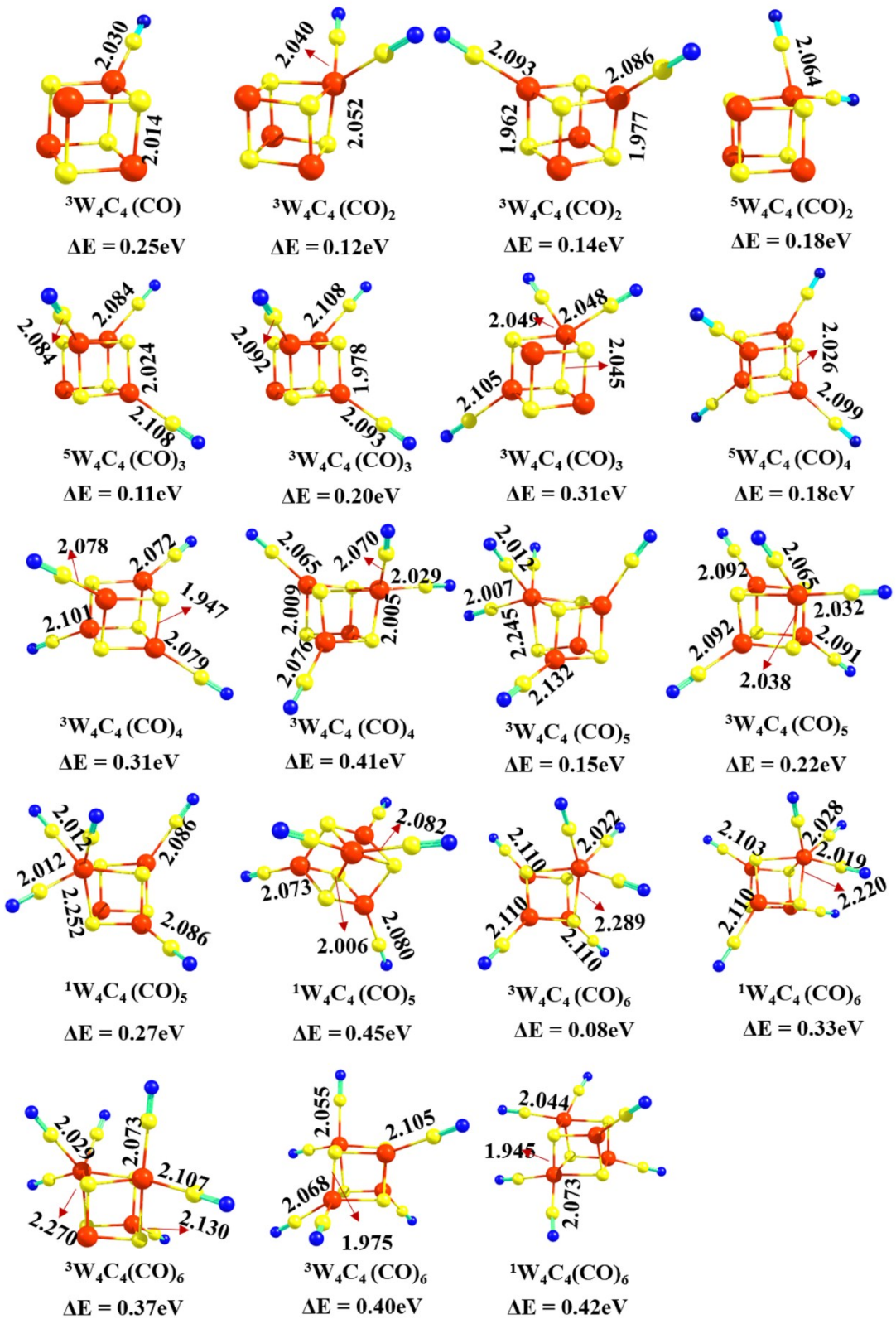

Fig. S3 The calculated low-lying isomers of the $W_4C_4(CO)_n$ (n = 1-6) clusters.

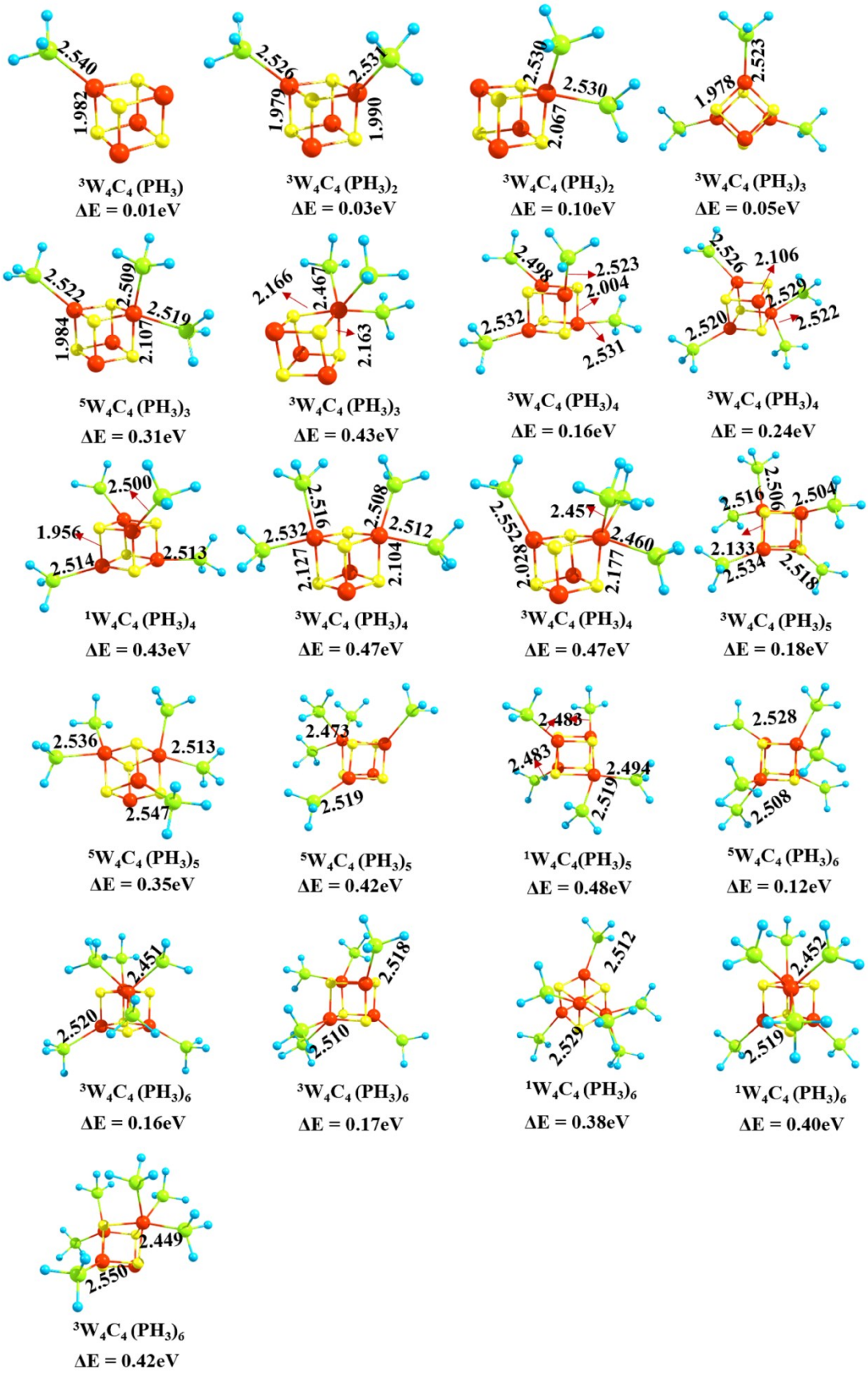

Fig. S4 The calculated low-lying isomers of the $W_4C_4(PH_3)_n$ (n = 1-6) clusters.

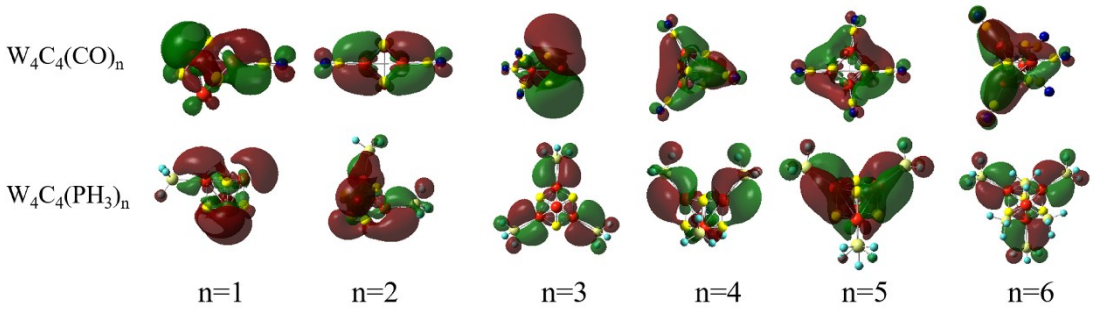

Fig. S5 Electron density isosurfaces for the HOMO of the lowest energy configurations of the $W_4C_4L_n$ (L = CO, PH_3; n = 1-6) clusters.

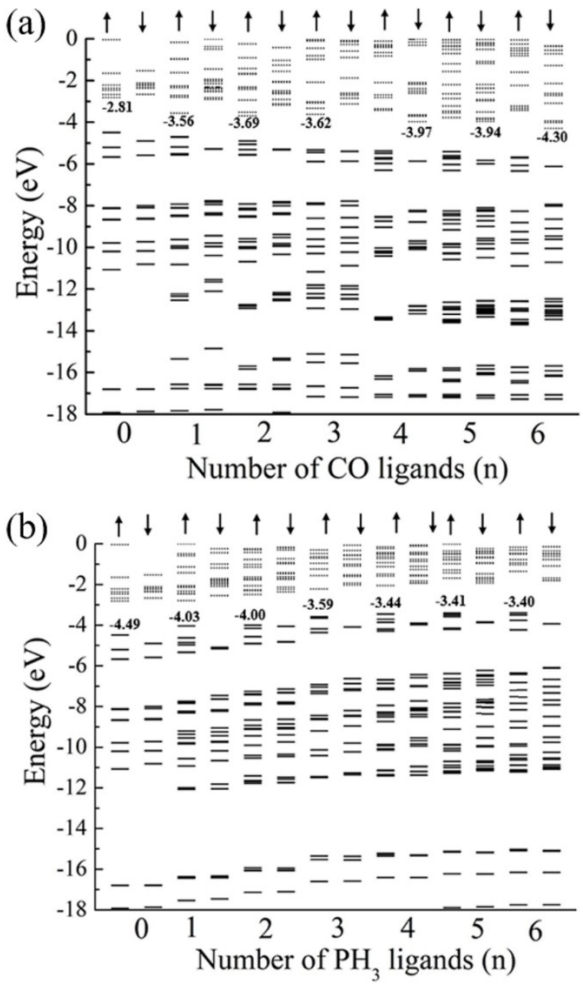

Fig. S6 One-electron energy levels of the $W_4C_4L_n$ (L = CO, PH_3; n = 0-6) clusters. The occupied and unoccupied states of the clusters are shown by solid and dashed lines, respectively. The majority and minority spin states of these open-shell clusters are indicated by up and down arrows. The theoretical values (in eV) of LUMO or HOMO states are listed.

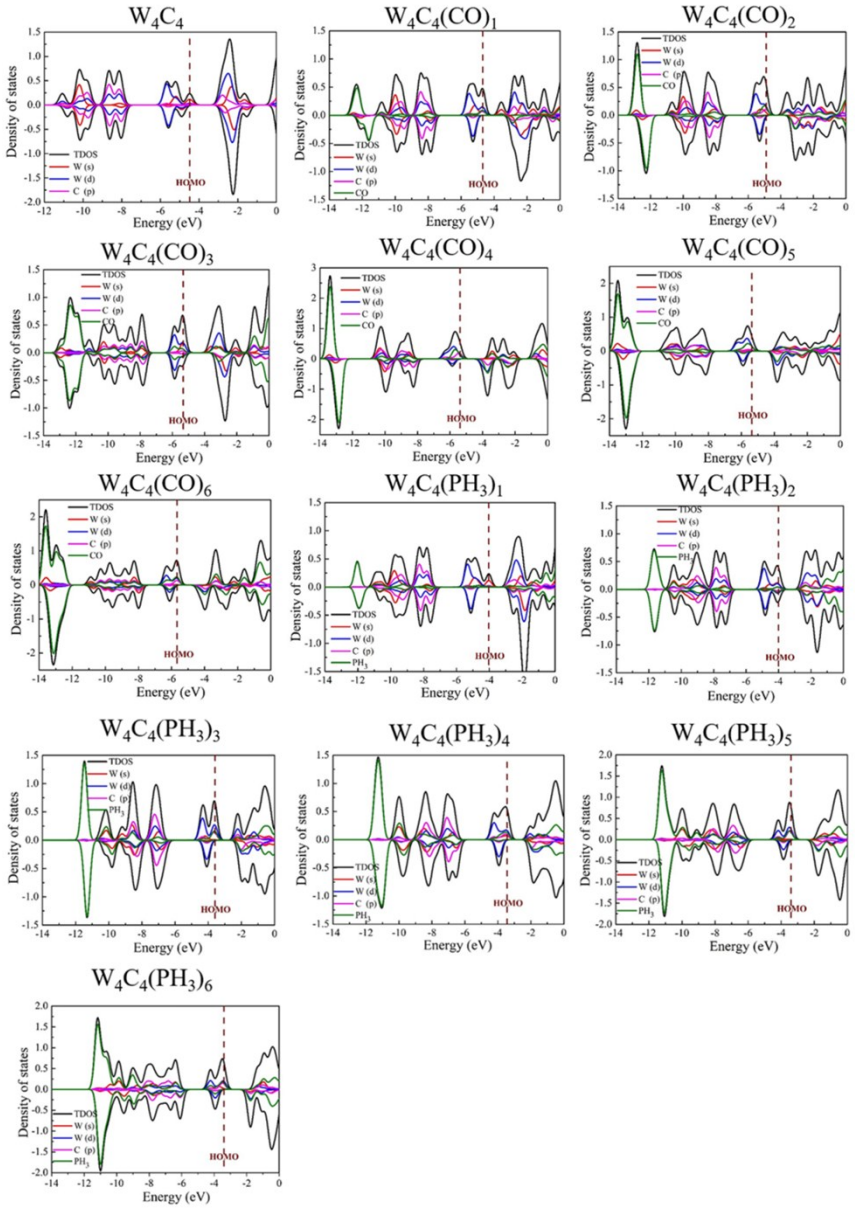

Fig. S7 TDOS and PDOS for the ground states of $W_4C_4L_n$ (L = CO, PH_3; n = 0-6). Lorentzian broadening of FWHM is 0.4 eV. The dotted lines refer to the position of the HOMOs.

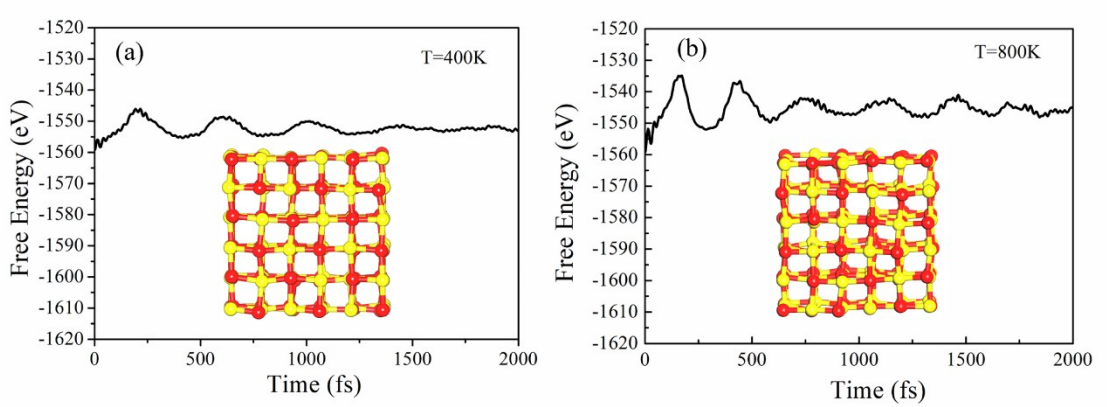

Fig. S8 Variations of total energy of the W_4C_4 cluster solid at (a) 400 and (b) 800 K during ab initio MD simulations. The insets show the equilibrium structures of the solid at different temperatures.