Supporting Information

for

Electrode Materials for NO Electroreduction Based on Dithiolene Metal–Organic Frameworks: A Theoretical Study

Jiake Fan, Lei Yang, Lixin Ye, Mengyun Mei and Weihua Zhu *

Institute for Computation in Molecular and Materials Science, School of Chemistry and Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China
* Correspondence: zhuwh@njust.edu.cn

Table S1. The cell information of $TM_3(THT)_2$ (TM=Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, Hf, Ta, W, Re, Os, Ir, Pt, Au).

	a/Å	b/Å	c/Å	alpha/°	beta/°	gamma/°
Sc	24.2308	24.2308	3.5252	90	90	120
Ti	23.8951	23.8951	3.4992			
V	23.7345	23.7345	3.4736			
Cr	23.6725	23.6725	3.4421			
Mn	23.655	23.655	3.4855			
Fe	23.5513	23.5513	3.4333			
Co	23.3401	23.3401	3.3756			
Ni	23.2498	23.2498	3.4061			
Cu	23.3567	23.3567	3.4692			
Zn	23.7656	23.7656	3.3735			
Y	24.8711	24.8711	3.5416			
Zr	24.4081	24.4081	3.5263			
Nb	24.188	24.188	3.4589			
Mo	23.9975	23.9975	3.4066			
Tc	23.839	23.839	3.3233			
Ru	23.7616	23.7616	3.2356			
Rh	23.7055	23.7055	3.2784			
Pd	23.7065	23.7065	3.3768			
Ag	23.9739	23.9739	3.4406			
Cd	24.4014	24.4014	3.3805			
Hf	24.2701	24.2701	3.4947			
Ta	24.12	24.12	3.4674			
W	23.9837	23.9837	3.4278			
Re	23.8565	23.8565	3.3528			
Os	23.7774	23.7774	3.2454			
Ir	23.7222	23.7222	3.2819			
Pt	23.6815	23.6815	3.3921			
Au	23.7383	23.7383	3.5404			

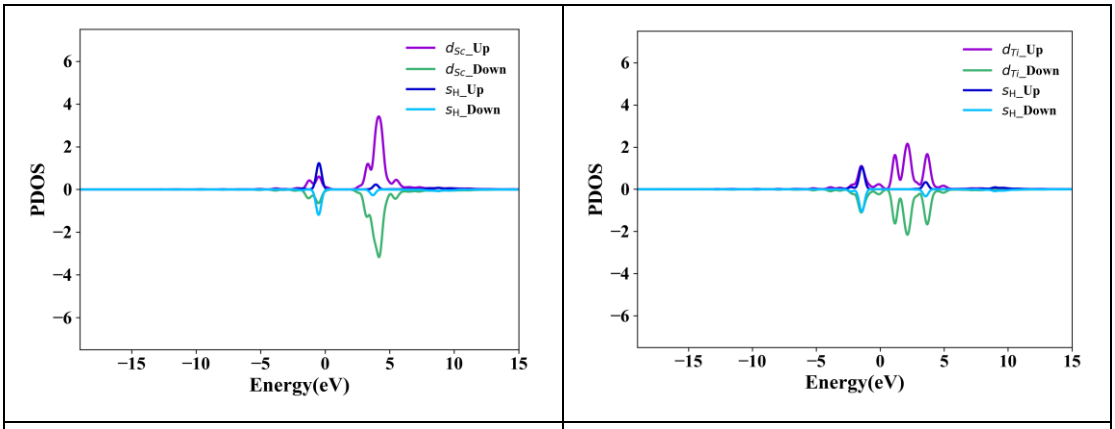
Table S2. Oxidation state of transition metal sites in $TM_3(THT)_2$ (TM=Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, Hf, Ta, W, Re, Os, Ir, Pt, Au)

Transition metal in $TM_3(THT)_2$	Oxidation state
Sc	3
Ti	4
V	4
Cr	4
Mn	4
Fe	4
Co	6
Ni	2
Cu	3
Zn	2
Y	4
Zr	4
Nb	4
Mo	4
Tc	4
Ru	4
Rh	3
Pd	2
Ag	1
Cd	2
Hf	4
Ta	6
W	4
Re	4
Os	4
Ir	4
Pt	2
Au	3

Table S3. Energy of $Ta_3(THT)_2$ and adsorbed intermediates under different transition metal spin states in HER and NORR process.

The initial guess of Ta's spin	$E_{Ta2(THT)3}$/Ha	$E_{Ta2(THT)3-H}$/Ha	$E_{Ta2(THT)3-NO}$/Ha
0	-6538.3878292	-6539.0449703	-6668.3326908
1	-6538.3878292	-6539.0449703	-6668.3326908
2	-6538.3878292	-6539.0449703	-6668.3326908
3	-6538.3878292	-6539.0449703	-6668.3326908
4	-6538.3878292	-6539.0449703	-6668.3326909
5	-6538.3878292	-6539.0449703	-6668.3326909
6	-6538.3878292	-6539.0449703	-6668.3326909
7	-6538.3878292	-6539.0449703	-6668.3326909
The initial guess of Ta's spin	$E_{Ta2(THT)3-NOH}$/Ha	$E_{Ta2(THT)3-N}$/Ha	$E_{Ta2(THT)3-NH}$/Ha
0	-6668.9252389	-6593.1092724	-6593.7857122
1	-6668.9252389	-6593.1092724	-6593.7857122
2	-6668.9252389	-6593.1092724	-6593.7857122
3	-6668.9252389	-6593.1092724	-6593.7857122
4	-6668.9252389	-6593.1092724	-6593.7857122
5	-6668.9252389	-6593.1092724	-6593.7857122
6	-6668.9252389	-6593.1092724	-6593.7857122
7	-6668.9252389	-6593.1092724	-6593.7857122

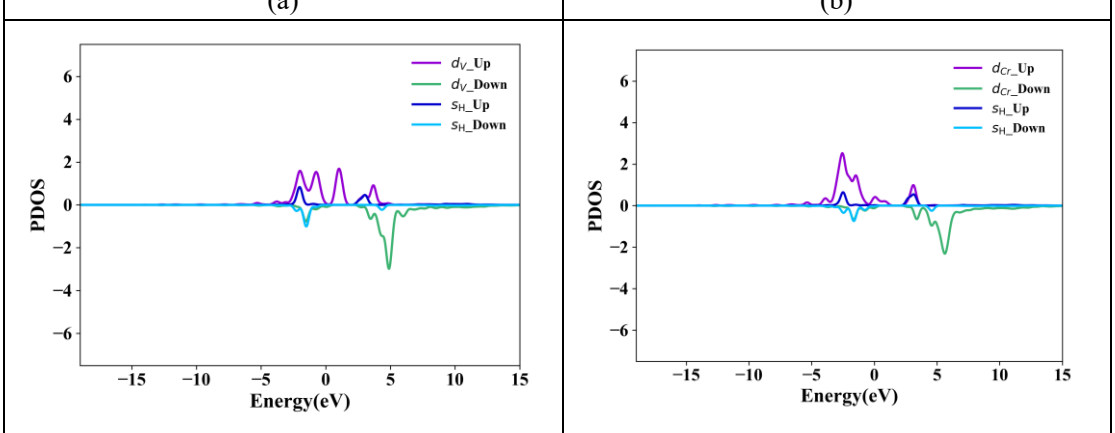
The initial guess of Ta's spin	$E_{Ta2(THT)3-NH2}$/Ha	$E_{Ta2(THT)3-NH3}$/Ha
0	-6594.4180483	-6595.0171315
1	-6594.4180483	-6595.0171315
2	-6594.4180483	-6595.0171315
3	-6594.4180483	-6595.0171315
4	-6594.4180483	-6595.0171313
5	-6594.4180483	-6595.0171313
6	-6594.4180483	-6595.0171313
7	-6594.4180483	-6595.0171313


d_{Sc}_Up
d_{Sc}_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

(a)

d_{Ti}_Up
d_{Ti}_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

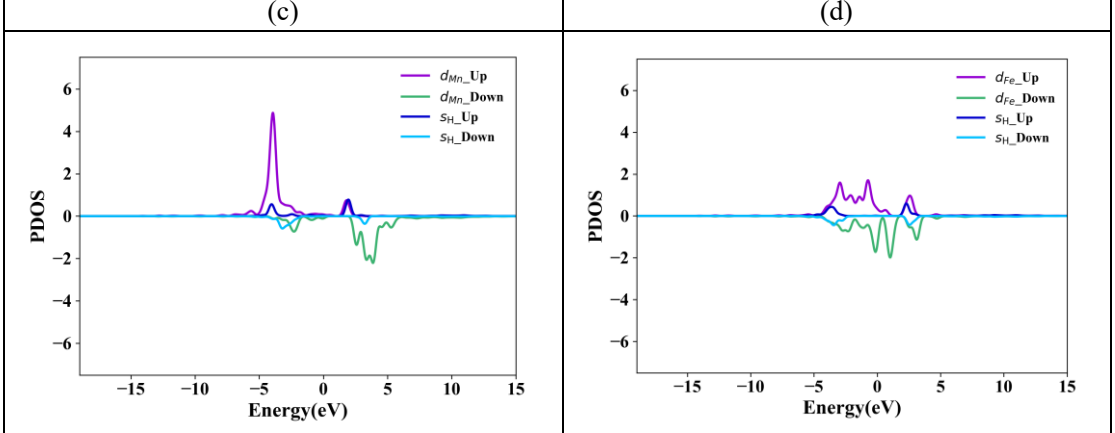
(b)


d_V_Up
d_V_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

(c)

d_{Cr}_Up
d_{Cr}_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

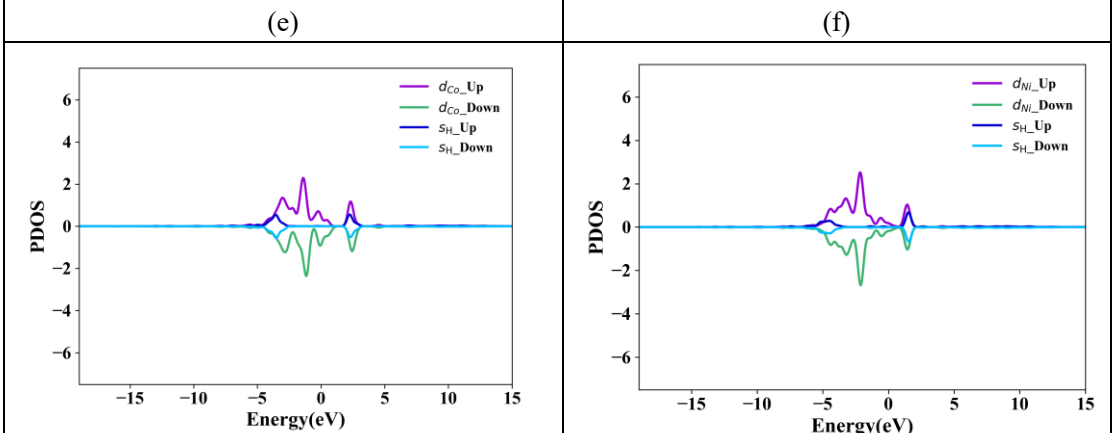
(d)


d_{Mn}_Up
d_{Mn}_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

(e)

d_{Fe}_Up
d_{Fe}_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

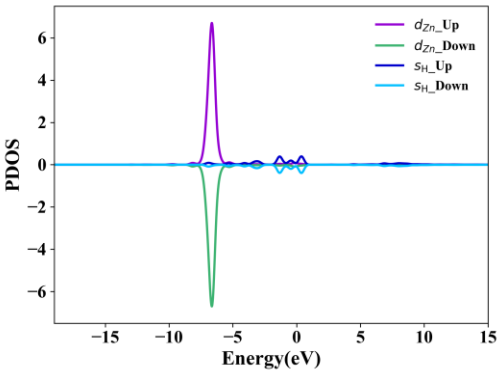
(f)


d_{Co}_Up
d_{Co}_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

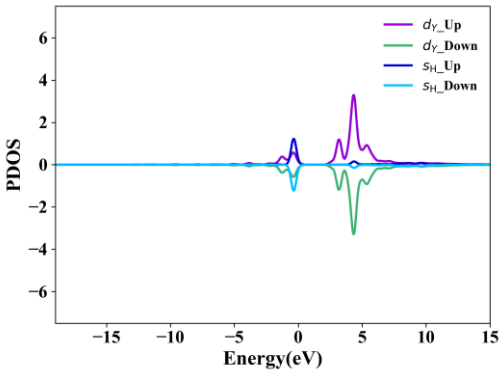
(g)

d_{Ni}_Up
d_{Ni}_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

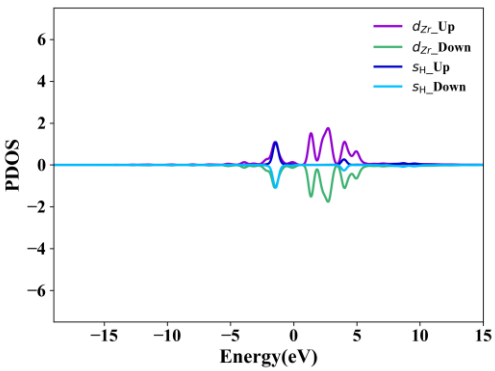
(h)


d_{Zn}_Up
d_{Zn}_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

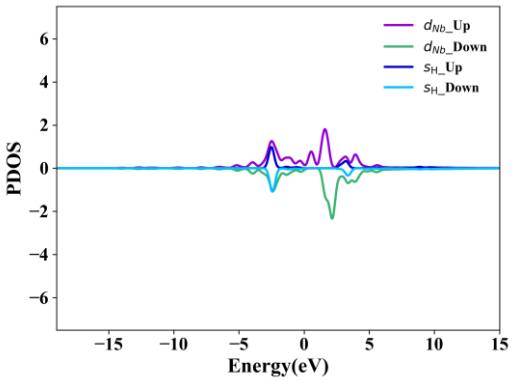
(i)


d_Y_Up
d_Y_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

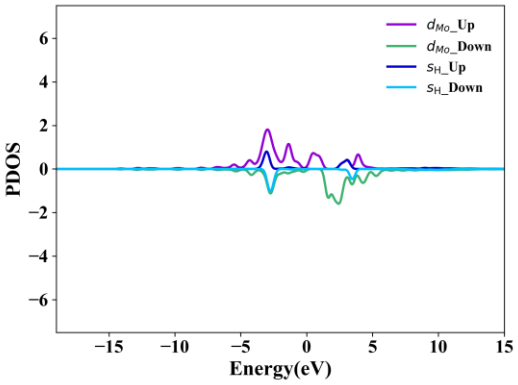
(j)


d_{Zr}_Up
d_{Zr}_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

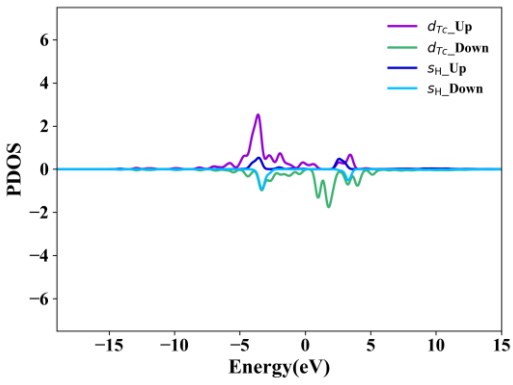
(k)


d_{Nb}_Up
d_{Nb}_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

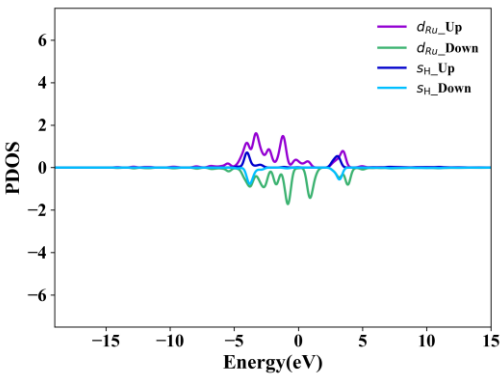
(l)


d_{Mo}_Up
d_{Mo}_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

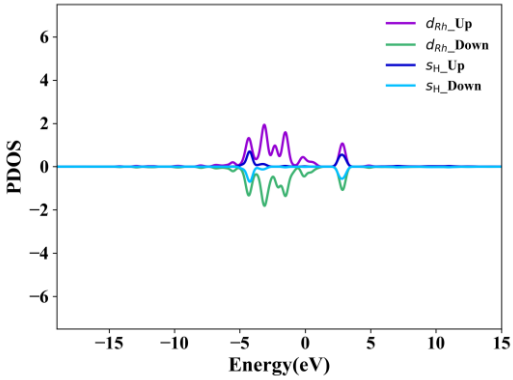
(m)


d_{Tc}_Up
d_{Tc}_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

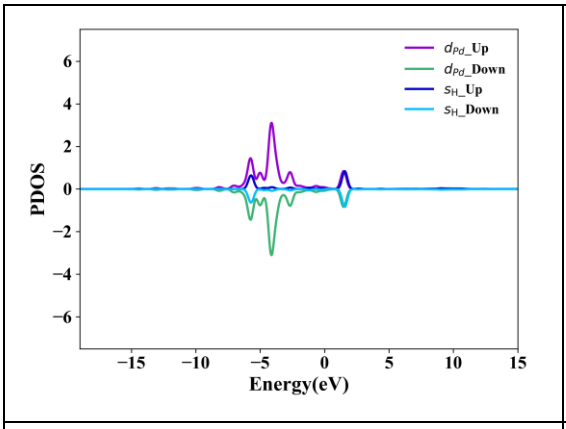
(n)


d_{Ru}_Up
d_{Ru}_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

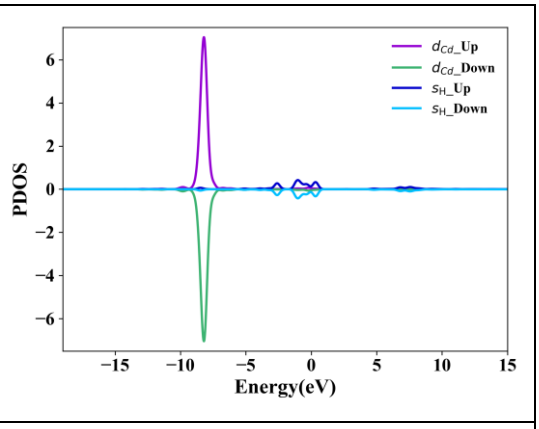
(o)


d_{Rh}_Up
d_{Rh}_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

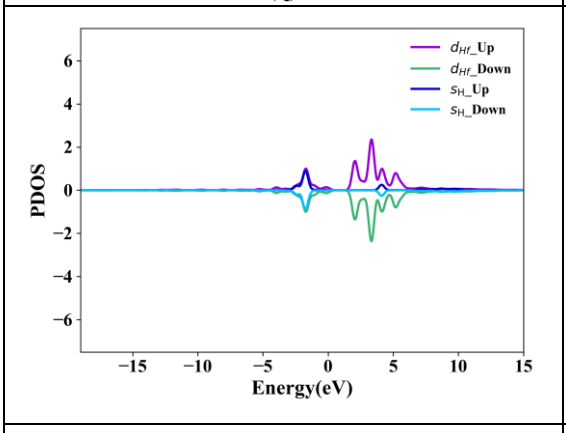
(p)


d_{Pd}_Up
d_{Pd}_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

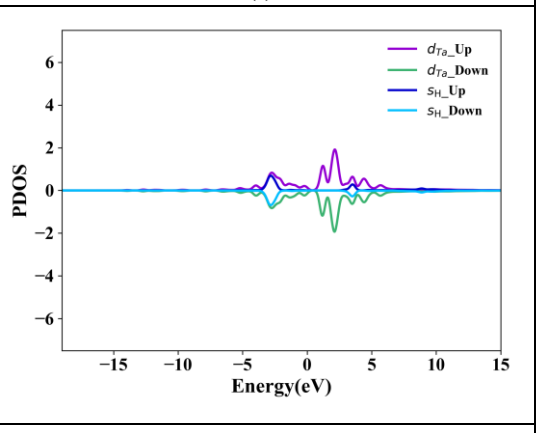
(q)


d_{Cd}_Up
d_{Cd}_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

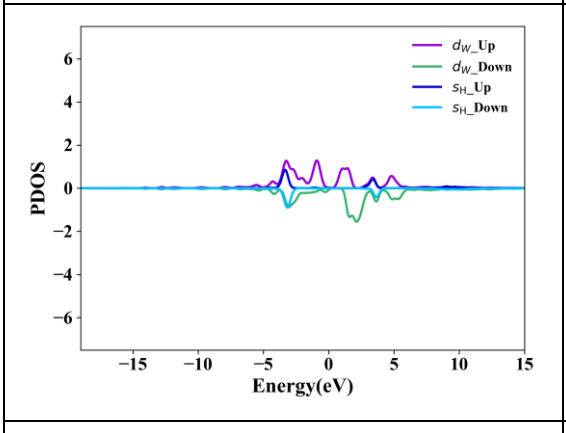
(r)


d_{Hf}_Up
d_{Hf}_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

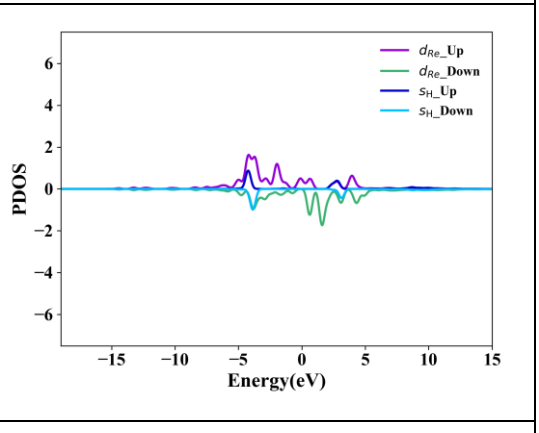
(s)


d_{Ta}_Up
d_{Ta}_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

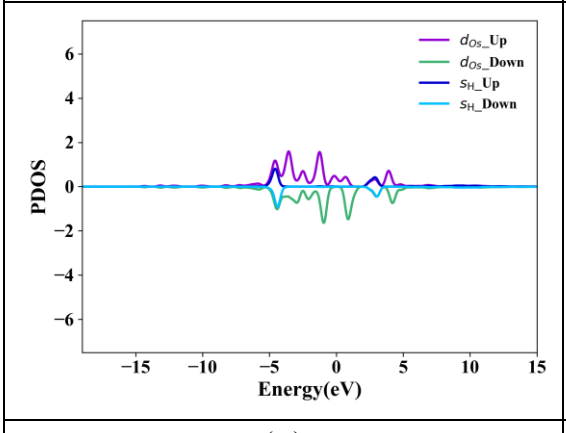
(t)


d_W_Up
d_W_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

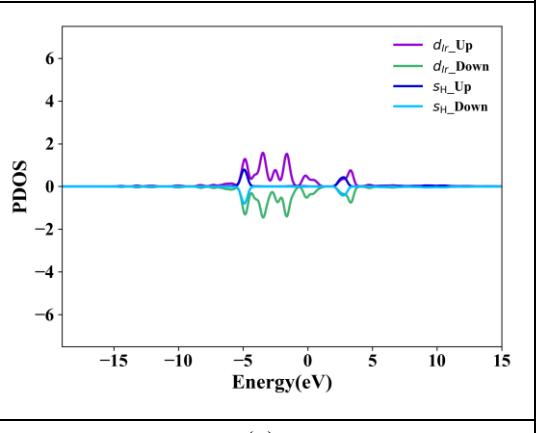
(u)


d_{Re}_Up
d_{Re}_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

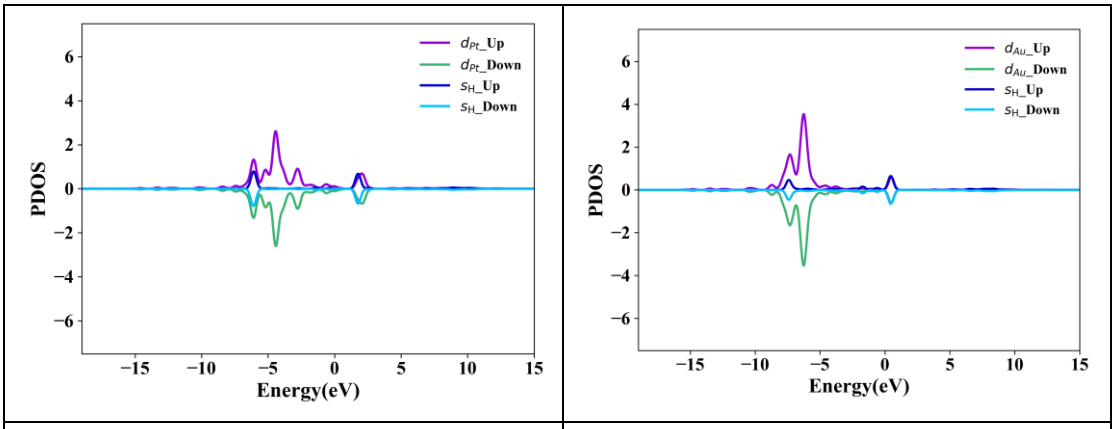
(v)


d_{Os}_Up
d_{Os}_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

(w)

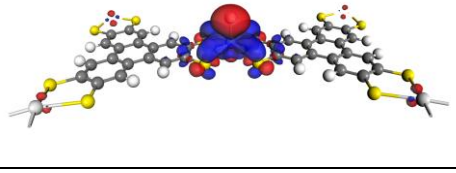
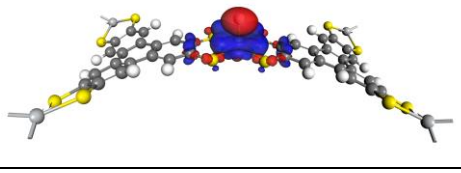
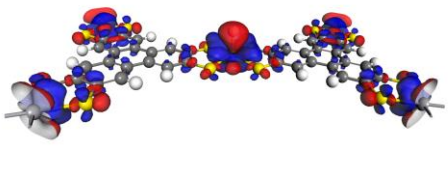
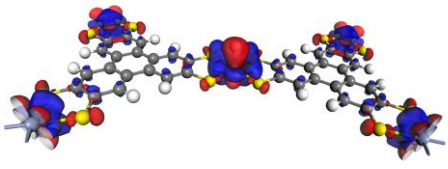
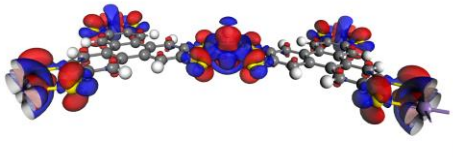
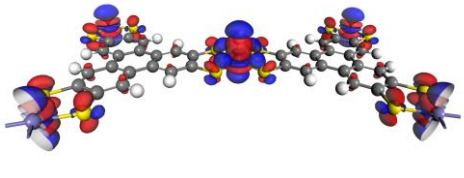
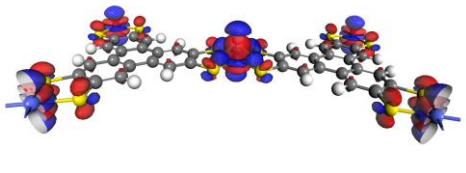
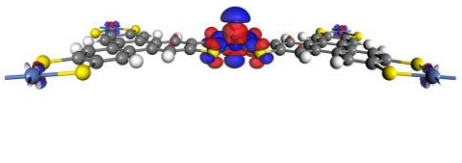
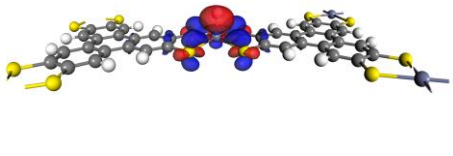
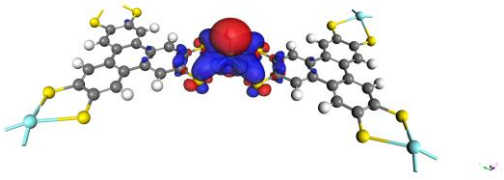
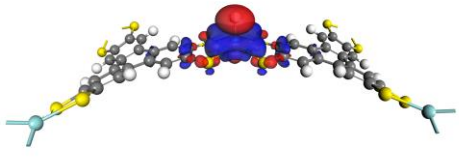
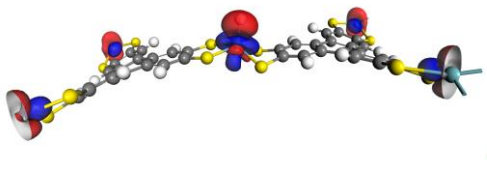

d_{Ir}_Up
d_{Ir}_Down
s_H_Up
s_H_Down
PDOS
Energy(eV)

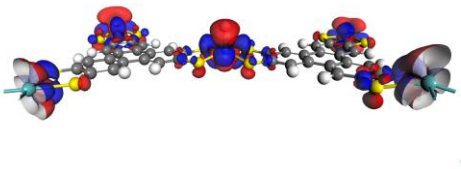
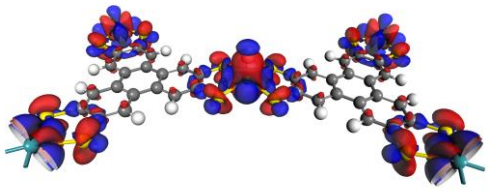
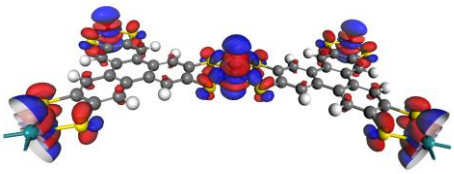
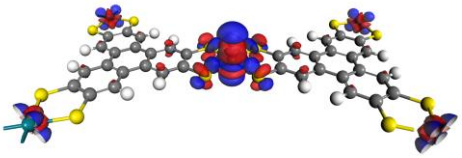
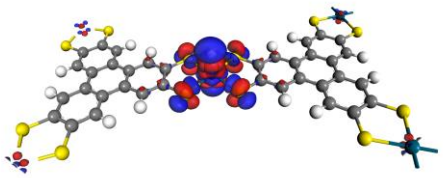
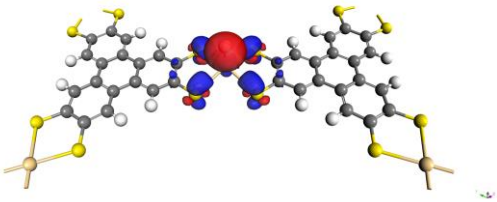
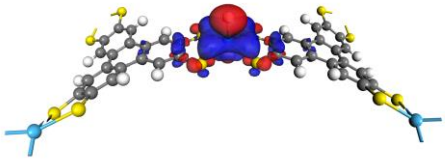
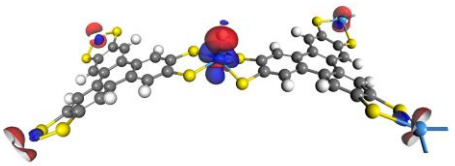
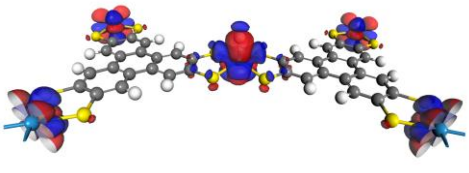
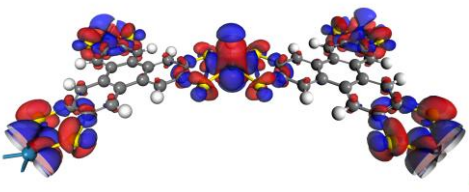
(x)



(y) (z)

Figure S1. Partial Density of States (PDOS) of transition metal and adsorbed hydrogen atom in hydrogen evolution reaction (HER) on $TM_3(THT)_2$

	
(a) Sc	(b) Ti
	
(c) V	(d) Cr
	
(e) Mn	(f) Fe
	
(g) Co	(h) Ni
	
(i) Zn	(j) Y
	
(k) Zr	(l) Nb

	
(m) Mo	(n) Tc
	
(o) Ru	(p) Rh
	
(q) Pd	(r) Cd
	
(s) Hf	(t) Ta
	
(u) W	(v) Re

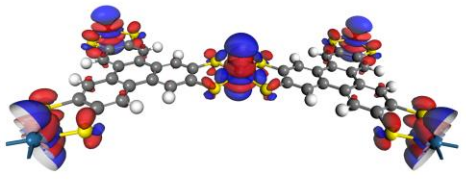
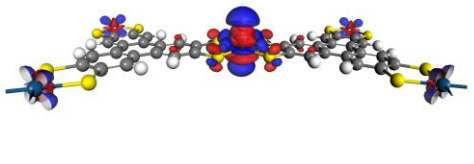
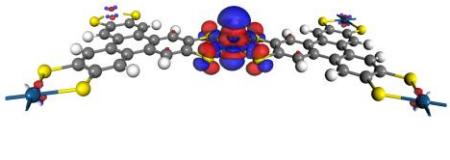
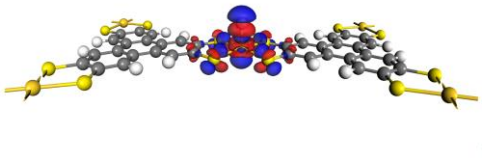
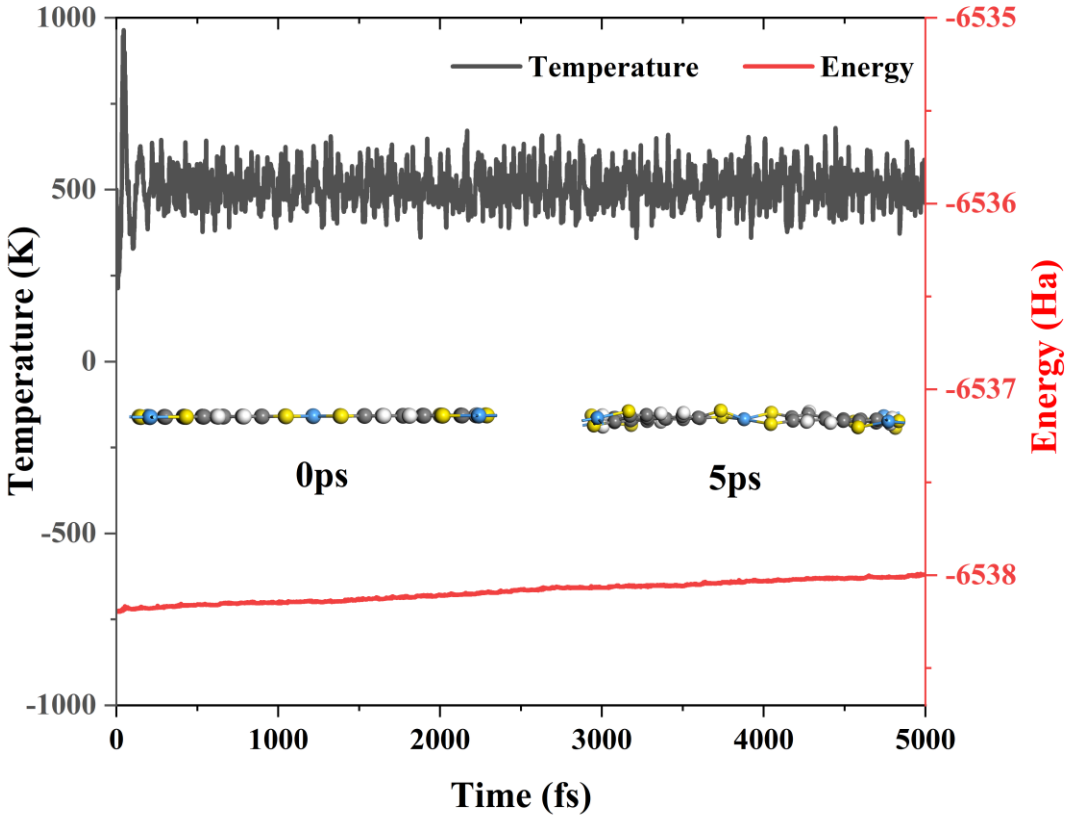
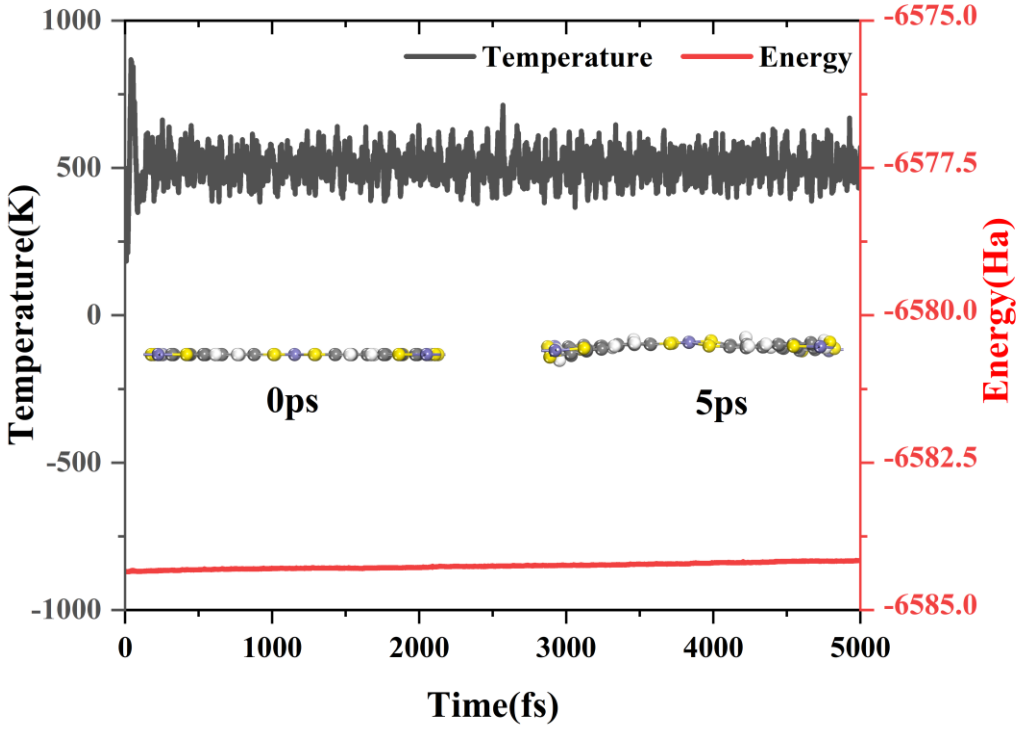
	
(w) Os	(x) Ir
	
(y) Pt	(z) Au

Figure S2. Electron density difference (EDD) of $TM_3(THT)_2$ under hydrogen evolution reaction (HER).

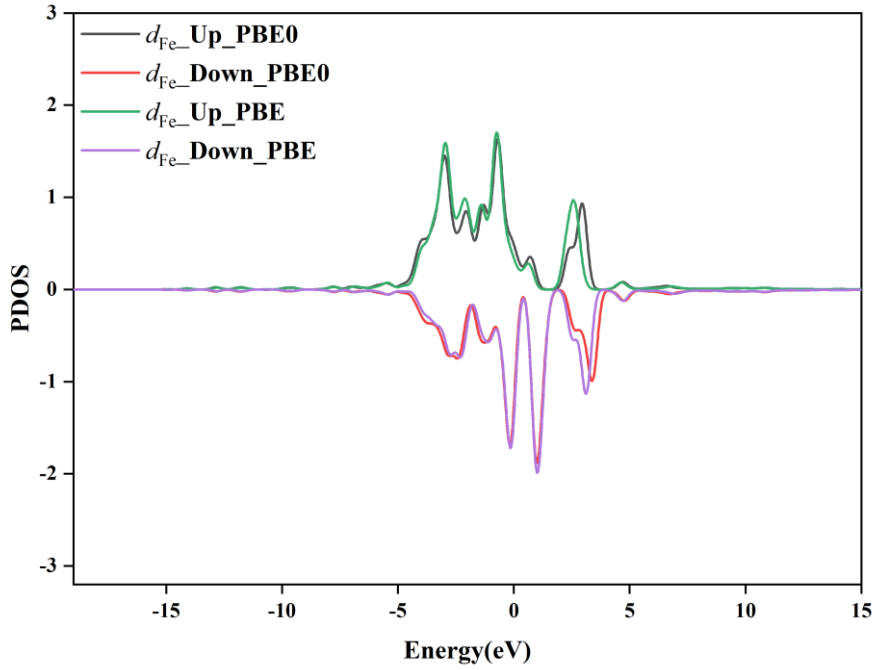


(a) $Fe_3(THT)_2$

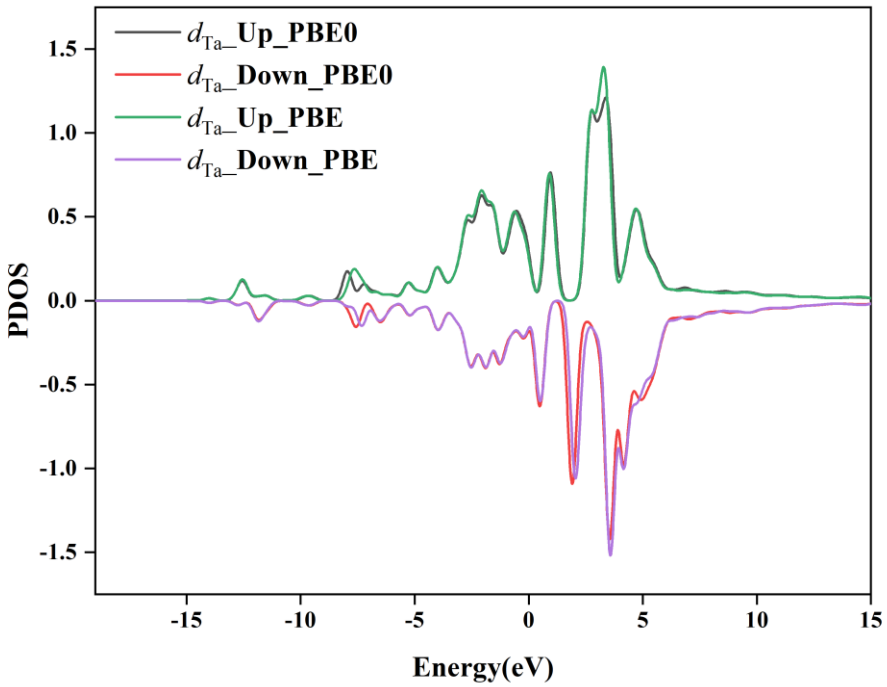


(b) $Ta_3(THT)_2$

Figure S3. Energy and temperature evolution curve of AIMD



(a)



(b)

Figure S4. Partial density of states of Fe when hydrogen atom was adsorbed on transition metal active sites of $Fe_3(THT)_2$ under PBE and PBE0 (a), Partial density of states of Ta when NO was adsorbed on $Ta_3(THT)_2$ under PBE and PBE0 (b).