Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for

Two-Dimensional π-Conjugated Metal-Organic Nanosheets as Single–Atom Catalysts for Hydrogen Evolution Reaction

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Table S1. The lattice constant ***a*** of every 2D MOF (M-X) configurations and the corresponding Gibbs adsorption free energies ΔG(*H) on the metal (M) sites.

M-N			M-S			M-Se			M-O		
M	***a*** (Å)	ΔG(*H) (eV)	M	***a*** (Å)	ΔG(*H) (eV)	M	***a*** (Å)	ΔG(*H) (eV)	M	***a*** (Å)	ΔG(*H) (eV)
Fe	13.52	0.17	Fe	14.81	0.20	Fe	15.47	0.21	Fe	13.16	0.71
Co	13.39	0.34	Co	14.67	0.09	Co	15.34	0.16	Co	13.03	0.33
Ni	13.35	1.34	Ni	14.63	0.80	Ni	15.29	0.45	Ni	12.98	1.36
Pd	13.85	1.45	Pd	15.05	0.77	Pd	15.70	0.57	Pd	13.49	1.36
Pt	13.89	1.10	Pt	15.05	0.50	Pt	15.70	0.29	Pt	13.53	0.79
Ru	13.93	-0.41	Ru	15.20	-0.56	Ru	15.82	-0.62	Ru	13.63	-0.11
Rh	13.90	0.02	Rh	15.07	-0.36	Rh	15.71	-0.32	Rh	13.57	-0.26
Ir	13.92	-0.12	Ir	15.16	-0.48	Ir	15.73	-0.47	Ir	13.57	-0.50
Os	13.90	-0.38	Os	15.19	-1.04	Os	15.56	-0.63	Os	13.63	-0.23

Table S2. The Gibbs adsorption free energies ΔG(*H) on the non-metal (X) sites of 2D MOF (M-X) configurations.

M-S		M-Se		M-O	
M	ΔG(*H) (eV)	M	ΔG(*H) (eV)	M	ΔG(*H) (eV)
Fe	0.48	Fe	0.78	Fe	0.35
Co	0.48	Co	0.90	Co	0.21
Ni	0.65	Ni	0.81	Ni	0.30
Pd	0.11	Pd	0.77	Pd	0.23
Pt	0.83	Pt	1.13	Pt	0.41
Ru	0.28	Ru	0.28	Ru	0.48
Rh	0.19	Rh	0.19	Rh	0.07
Os	-0.24	Os	1.20	Os	0.71
Ir	0.54	Ir	0.54	Ir	0.22

Table S3. The strain effect of 2D Rh-N nanosheets on the Gibbs adsorption free energy ΔG(*H).

Strain	-3%	-2%	-1%	0%	1%	2%	3%
Lattice constant (Å)	13.483	13.622	13.761	13.900	14.039	14.178	14.317
ΔG(*H) (eV)	0.03	0.03	0.02	0.02	0.01	0.00	0.00

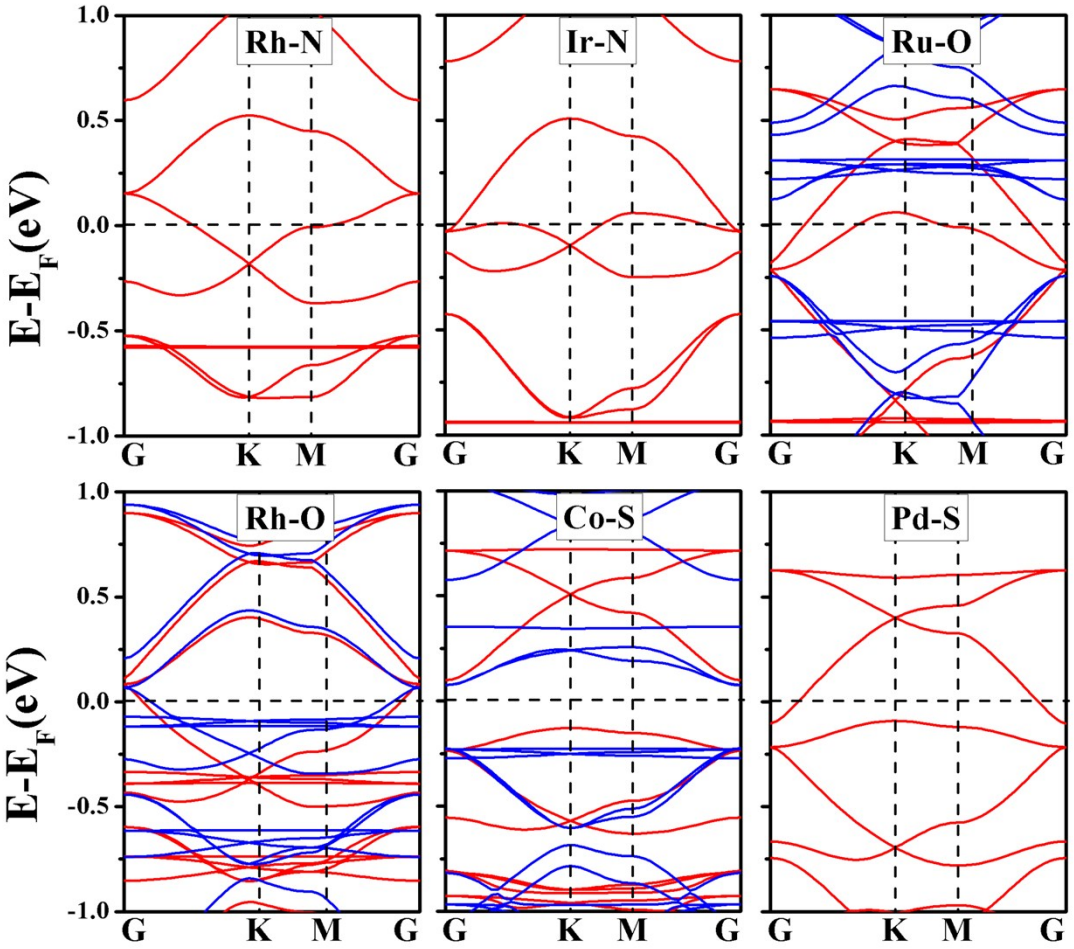

Figure S1. The band structures of six MOF configurations (a) Rh-N, (b) Ir-N, (c) Ru-O, (d) Rh-O, (e) Co-S and (f) Pd-S.

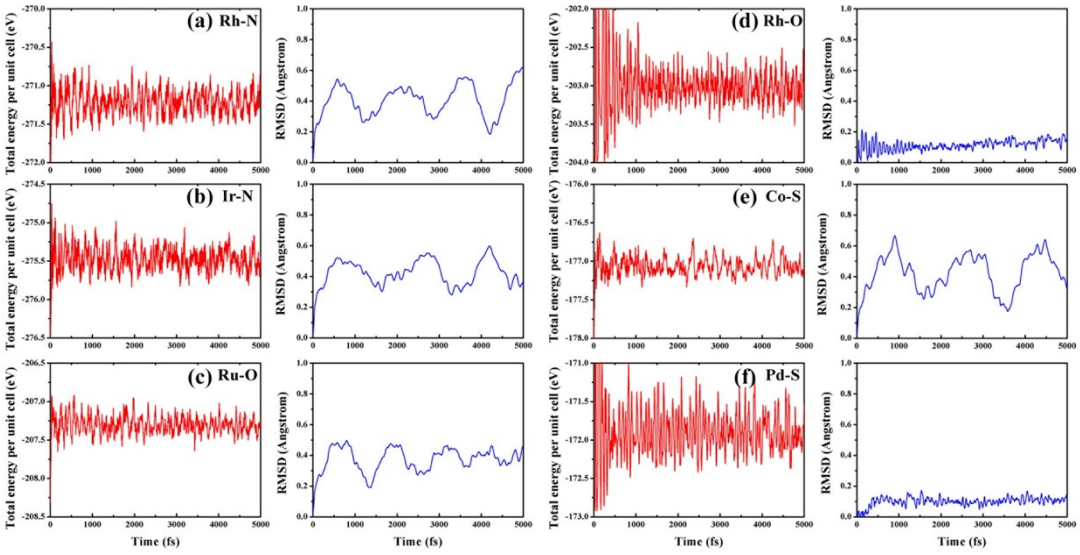

Figure S2. Total energy evolution and the corresponding root mean square deviation (RMSD) during 5000 fs first-principles molecular trajectories of the 2×2 supercells of six MOF configurations (a) Rh-N, (b) Ir-N, (c) Ru-O, (d) Rh-O, (e) Co-S and (f) Pd-S.

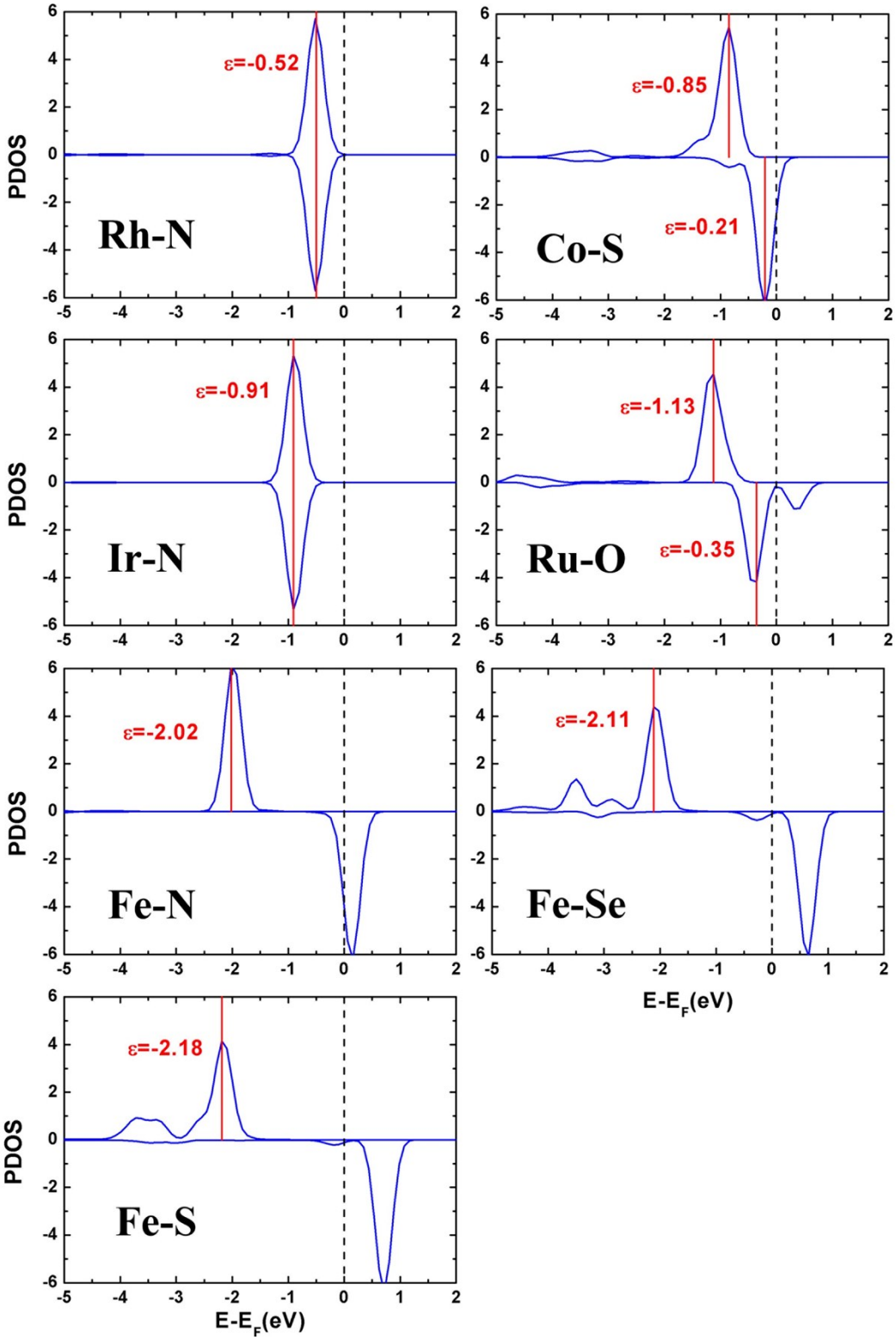

Figure S3. The projected density of state of the dz^2 orbital for the active metal sites in the Rh-N, Co-S, Ir-N, Ru-O. Fe-N, Fe-Se and Fe-S nanosheets.