Supporting information

First-principles design of bifunctional oxygen reduction and evolution catalysts through bimetallic centers in metal-organic frameworks

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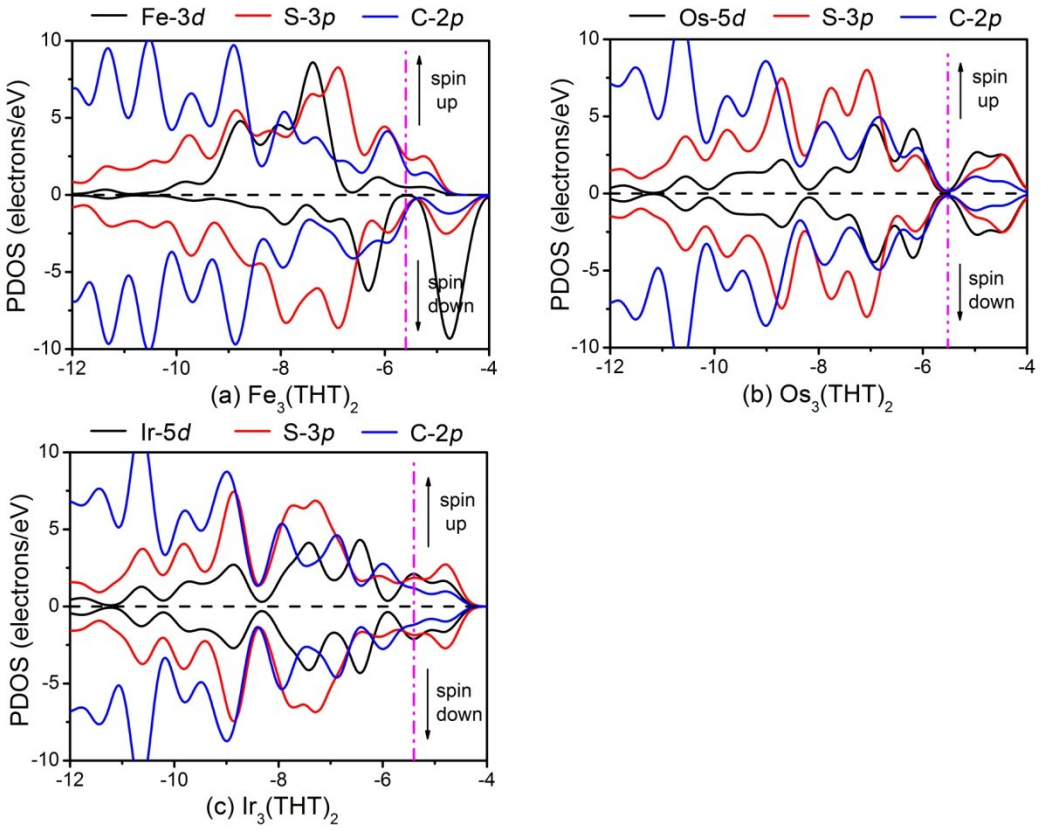

Fig. S1. Partial density of states (PDOS) of (a) $Fe_3(THT)_2$, (b) $Os_3(THT)_2$, and (c) $Ir_3(THT)_2$.

Table S1. Adsorption energy (E_{ad}) values of ORR intermediates and d-band center of $M_3(THT)_2$ nanosheets. All results are in the unit of eV. The corresponding adsorption structures are shown in Fig. S2.

E_{ad}	OOH	O	OH	ε_d
Fe	1.36	3.92	2.51	-1.23
Ru	1.76	4.86	2.35	-1.88
Os	1.96	5.59	3.18	-2.05
Co	0.87	3.77	2.07	-1.56
Rh	0.96	4.03	2.08	-2.13
Ir	0.95	3.91	2.18	-2.59
Ni	0.51	3.68	1.93	-1.88
Pd	0.64	3.74	2.05	-2.62
Pt	0.49	3.63	1.90	-3.01
Fe/Fe_2Co	1.37	3.95	2.52	-1.14
Co/Fe_2Co	0.89	3.56	2.07	-1.56
$Fe/FeCo_2$	1.37	3.98	2.58	-1.15
$Co/FeCo_2$	0.86	3.75	2.02	-1.57

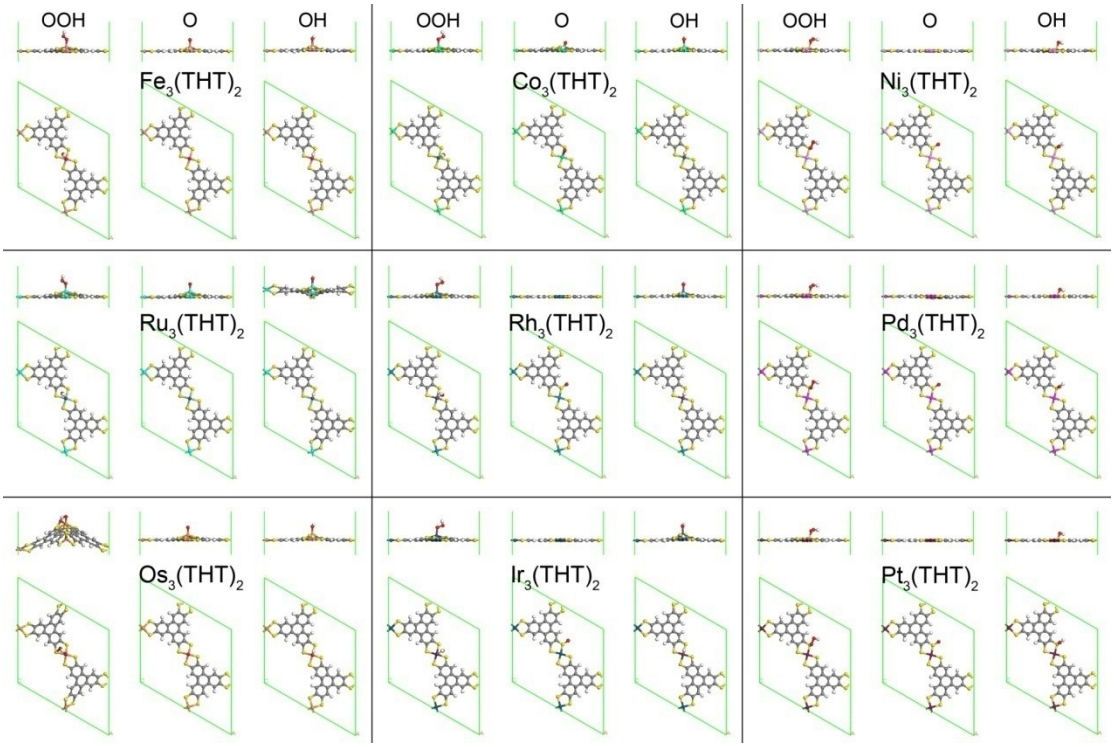

Fig. S2. Favorable adsorption structures of ORR intermediates on single-metal $M_3(THT)_2$ nanosheets.

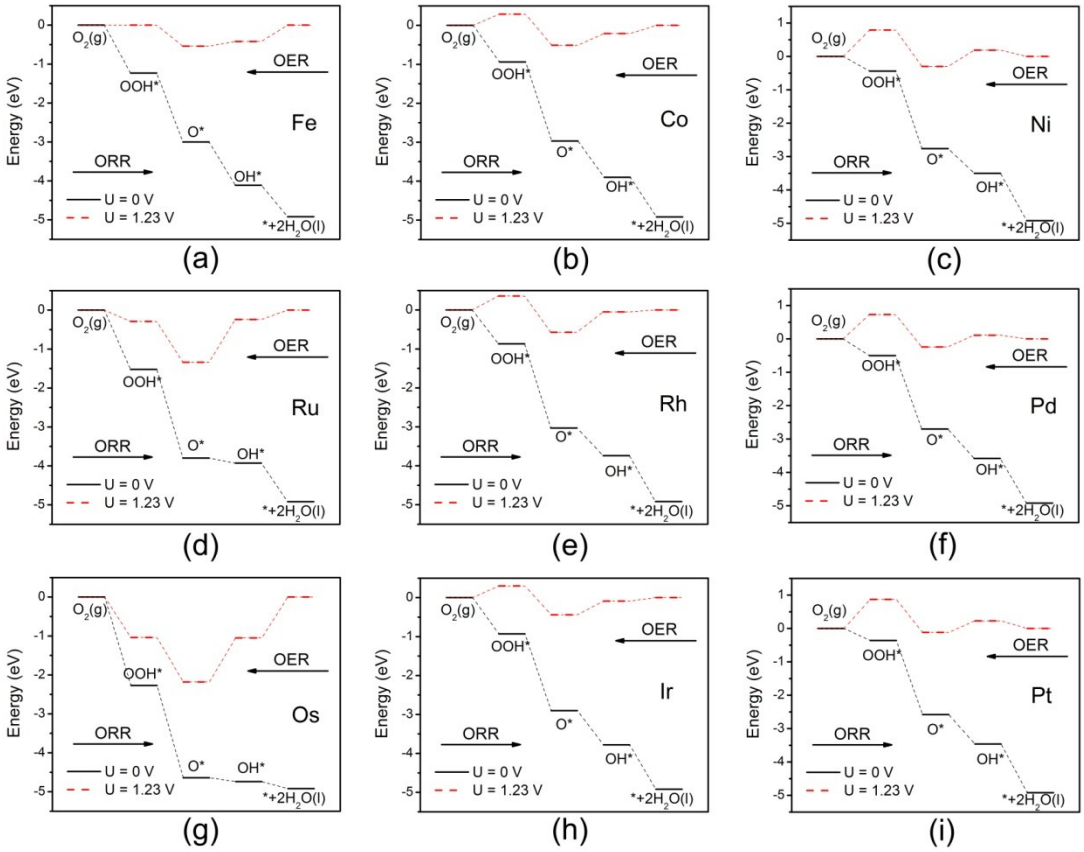

Fig. S3. Schematic free energy diagrams for ORR/OER on single-metal $M_3(THT)_2$ nanosheets.

Table S2. Mulliken charge analysis for $Fe_3(THT)_2$, $Co_3(THT)_2$, $Fe_2Co(THT)_2$ and $FeCo_2(THT)_2$ in units of *e*.

	Fe	S-Fe[a]	Co	S-Co[a]
$Fe_3(THT)_2$	0.425	–0.233		
$Co_3(THT)_2$			0.147	–0.161
$Fe_2Co(THT)_2$	0.424	–0.234	0.148	–0.161
$FeCo_2(THT)_2$	0.419	–0.233	0.147	–0.161

[a] S-Fe and S-Co indicate the S atoms bonded with Fe or Co atoms.

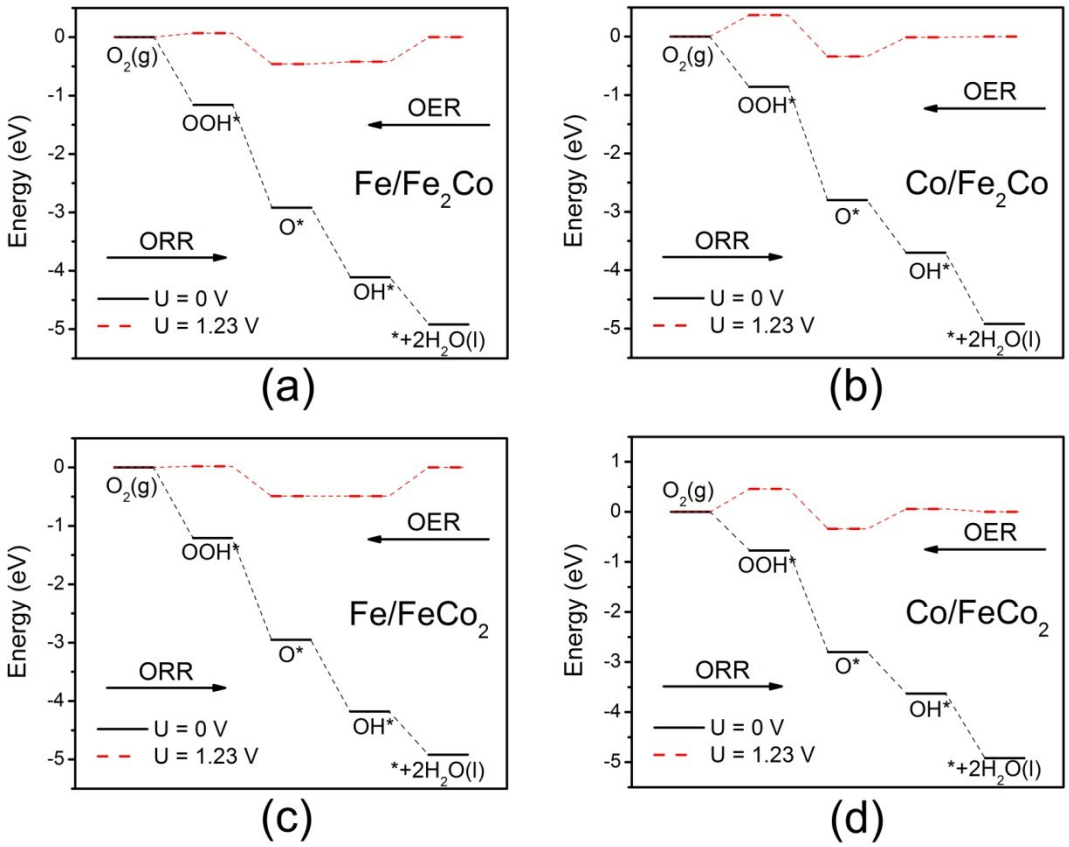

Fig. S4. Schematic free energy diagrams for ORR/OER on $Fe_xCo_{3-x}(THT)_2$ nanosheets.

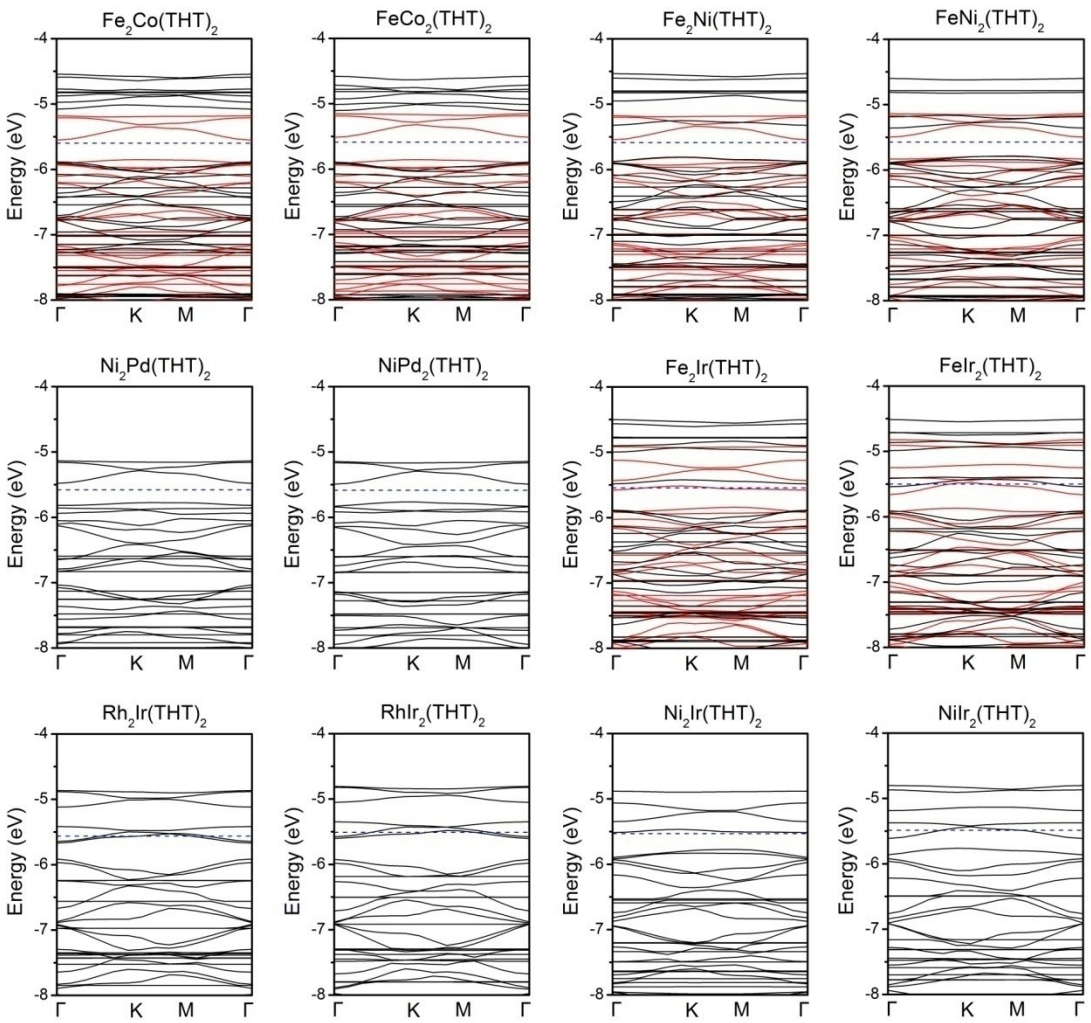

Fig. S5. The band structures of bi-metal $M_3(THT)_2$ nanosheets.

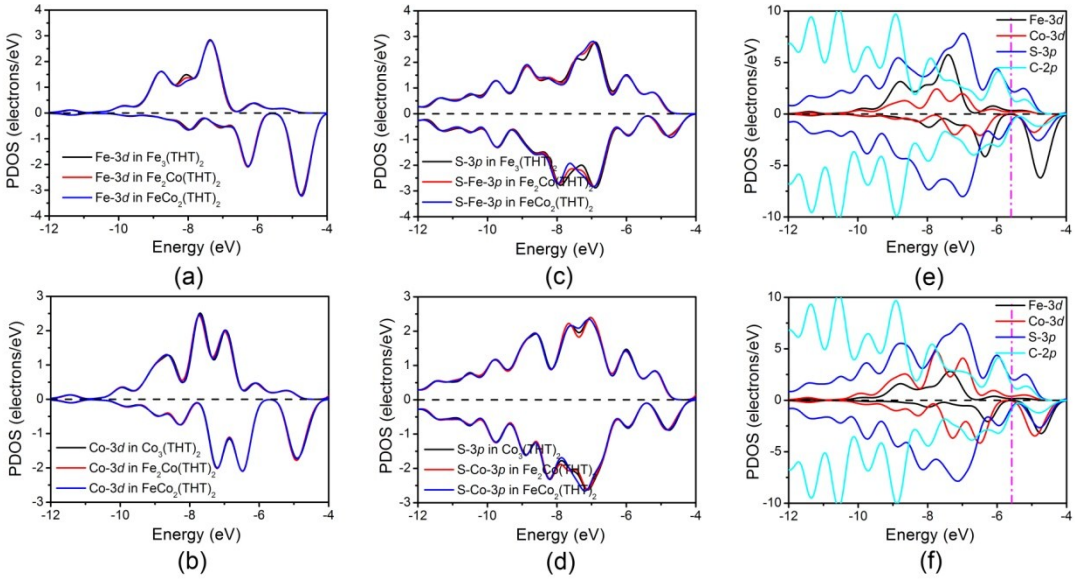

Fig. S6. Partial density of states (PDOS) of (a) Fe-3*d* in $Fe_3(THT)_2$, $Fe_2Co(THT)_2$, and $FeCo_2(THT)_2$, (b) Co-3*d* in $Co_3(THT)_2$, $Fe_2Co(THT)_2$, and $FeCo_2(THT)_2$, (c) S-3*p* of S atoms bonded with Fe atoms in $Fe_3(THT)_2$, $Fe_2Co(THT)_2$, and $FeCo_2(THT)_2$, (d) S-3*p* of S atoms bonded with Co atoms in $Co_3(THT)_2$, $Fe_2Co(THT)_2$, and $FeCo_2(THT)_2$, (e) $Fe_2Co(THT)_2$, and (f) $FeCo_2(THT)_2$.

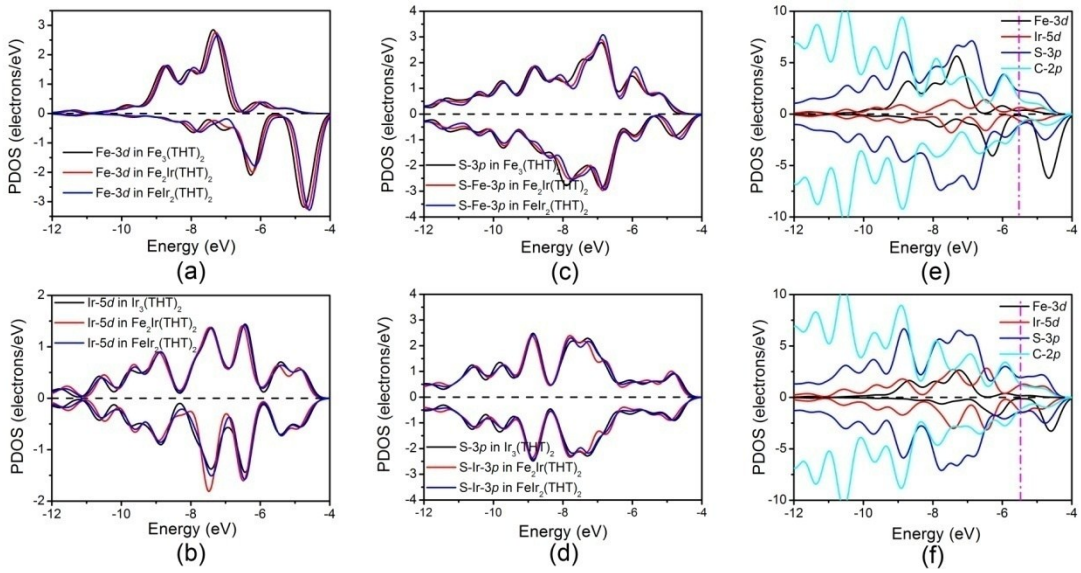

Fig. S7. Partial density of states (PDOS) of (a) Fe-3*d* in $Fe_3(THT)_2$, $Fe_2Ir(THT)_2$, and $FeIr_2(THT)_2$, (b) Ir-5*d* in $Ir_3(THT)_2$, $Fe_2Ir(THT)_2$, and $FeIr_2(THT)_2$, (c) S-3*p* of S atoms bonded with Fe atoms in $Fe_3(THT)_2$, $Fe_2Ir(THT)_2$, and $FeIr_2(THT)_2$, (d) S-3*p* of S atoms bonded with Co atoms in $Ir_3(THT)_2$, $Fe_2Ir(THT)_2$, and $FeIr_2(THT)_2$, (e) $Fe_2Ir(THT)_2$, and (f) $FeIr_2(THT)_2$.

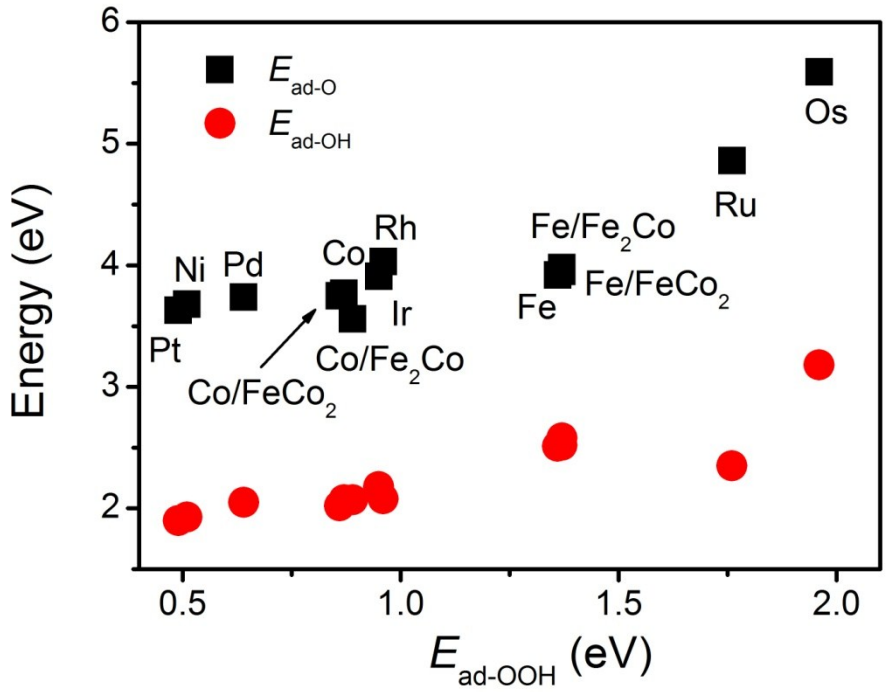

Fig. S8. Adsorption energies (E_{ad}) of O and OH plotted against the E_{ad} of OOH on $M_3(THT)_2$ nanosheets.