Electronic Supplementary Information (ESI) of

Computational screening of efficient azafullerene-supported single atom as bifunctional electrocatalysts for oxygen evolution and reduction reaction

Mo Xiong*, Tao Yang*

[1]MOE Key Laboratory for Non-Equilibrium Synthesis and Modulation of Condensed Matter, School of Physics, Xi'an Jiaotong University, Xi'an 710049, Shaanxi, China

Mo Xiong: xiongmo@xjtu.edu.cn
Tao Yang: taoyang1@xjtu.edu.cn

Table S1. Binding, cohesive energies of single TM, and their differences on $C_{54}N_4$-pyrid.

TM	E_b (eV)	E_{coh} (eV)	$E_b - E_{coh}$ (eV)
Fe	-6.485	-4.28	-2.205
Co	-6.815	-4.39	-2.425
Ni	-6.49	-4.44	-2.05
Ru	-7.49	-6.74	-0.75
Rh	-6.712	-5.75	-0.962
Pd	-4.283	-3.89	-0.393
Os	-7.957	-8.17	0.213
Ir	-7.646	-6.94	-0.706
Pt	-6.024	-5.84	-0.184
Ti	-7.526	-4.85	-2.676
V	-6.201	-5.31	-0.891
Cr	-5.959	-4.1	-1.859
Mn	-5.412	-2.92	-2.492
Cu	-4.144	-3.49	-0.654
Zn	-2.77	-1.35	-1.42
Au	-1.884	-3.81	1.926
Zr	-8.207	-6.25	-1.957
Nb	-7.306	-7.57	0.264
Mo	-4.954	-6.82	1.866
Hf	-8.195	-6.44	-1.755
Ta	-8.102	-8.1	-0.002
W	-6.416	-8.9	2.484
Sc	-6.906	-3.9	-3.006
Y	-6.714	-4.37	-2.344
Cd	-1.523	-1.16	-0.363
Ag	-2.588	-2.95	0.362
Re	-4.853	-8.03	3.177

Table S2. Binding, cohesive energies of single TM, and their differences on $C_{54}N_4$-pyrid-pyrro.

M	E_b (eV)	E_{coh} (eV)	$E_b - E_{coh}$ (eV)

Fe	-7.319	-4.28	-3.039
Co	-7.541	-4.39	-3.151
Ni	-7.485	-4.44	-3.045
Ru	-7.818	-6.74	-1.078
Rh	-7.371	-5.75	-1.621
Pd	-5.435	-3.89	-1.545
Os	-8.312	-8.17	-0.142
Ir	-8.354	-6.94	-1.414
Pt	-7.257	-5.84	-1.417
Ti	-9.191	-4.85	-4.341
V	-8.432	-5.31	-3.122
Cr	-7.014	-4.1	-2.914
Mn	-6.489	-2.92	-3.569
Cu	-5.244	-3.49	-1.754
Zn	-3.961	-1.35	-2.611
Au	-3.38	-3.81	0.43
Zr	-8.752	-6.25	-2.502
Nb	-7.553	-7.57	0.017
Mo	-7.22	-6.82	-0.4
Hf	-8.727	-6.44	-2.287
Ta	-9.678	-8.1	-1.578
W	-8.538	-8.9	0.362
Sc	-9.341	-3.9	-5.441
Y	-7.868	-4.37	-3.498
Cd	-2.674	-1.16	-1.514
Ag	-3.044	-2.95	-0.094
Re	-7.449	-8.03	0.581

Table S3. Binding, cohesive energies of single TM, and their differences on $C_{64}N_4$-pyrid.

M	E_b (eV)	E_{coh} (eV)	$E_b - E_{coh}$ (eV)
Fe	-6.394	-4.28	-2.114

Co	-6.68	-4.39	-2.29
Ni	-6.366	-4.44	-1.926
Ru	-7.342	-6.74	-0.602
Rh	-6.555	-5.75	-0.805
Pd	-4.129	-3.89	-0.239
Os	-7.773	-8.17	0.397
Ir	-7.477	-6.94	-0.537
Pt	-5.855	-5.84	-0.015
Ti	-7.66	-4.85	-2.81
V	-6.088	-5.31	-0.778
Cr	-5.876	-4.1	-1.776
Mn	-5.366	-2.92	-2.446
Cu	-4.041	-3.49	-0.551
Zn	-2.635	-1.35	-1.285
Au	-1.76	-3.81	2.05
Zr	-8.259	-6.25	-2.009
Nb	-7.236	-7.57	0.334
Mo	-4.817	-6.82	2.003
Hf	-8.265	-6.44	-1.825
Ta	-8.038	-8.1	0.062
W	-6.18	-8.9	2.72
Sc	-6.825	-3.9	-2.925
Y	-6.511	-4.37	-2.141
Cd	-1.404	-1.16	-0.244
Ag	-2.526	-2.95	0.424
Re	-4.581	-8.03	3.449

Table S4. Binding, cohesive energies of single TM, and their differences on $C_{64}N_4$-pyrid-pyrro.

M	E_b (eV)	E_{coh} (eV)	$E_b - E_{coh}$ (eV)
Fe	-8.325	-4.28	-4.045

Co	-8.499	-4.39	-4.109
Ni	-8.461	-4.44	-4.021
Ru	-8.833	-6.74	-2.093
Rh	-8.343	-5.75	-2.593
Pd	-6.599	-3.89	-2.709
Os	-9.542	-8.17	-1.372
Ir	-9.602	-6.94	-2.662
Pt	-8.584	-5.84	-2.744
Ti	-10.038	-4.85	-5.188
V	-9.259	-5.31	-3.949
Cr	-7.82	-4.1	-3.72
Mn	-7.573	-2.92	-4.653
Cu	-6.019	-3.49	-2.529
Zn	-4.563	-1.35	-3.213
Au	-4.513	-3.81	-0.703
Zr	-9.728	-6.25	-3.478
Nb	-9.937	-7.57	-2.367
Mo	-8.208	-6.82	-1.388
Hf	-9.663	-6.44	-3.223
Ta	-10.784	-8.1	-2.684
W	-9.731	-8.9	-0.831
Sc	-10.204	-3.9	-6.304
Y	-8.868	-4.37	-4.498
Cd	-3.142	-1.16	-1.982
Ag	-2.18	-2.95	0.77
Re	-7.147	-8.03	0.883

Table S5. The adsorption Gibbs free energies (eV) and the bond length (Å) of reaction intermediates of OH, O and OOH, overpotentials (V) of OER and ORR on TM@$C_{54}N_4$-pyrid.

TM	ΔG_{*OH}	ΔG_{*O}	ΔG_{*OOH}	η_{OER}	η_{ORR}	M-O	M-OH	M-OOH

Fe	0.173	1.222	3.311	0.859	1.057	1.638	1.829	1.755
Co	0.957	2.101	3.914	0.583	0.273	1.654	1.865	1.855
Ni	1.383	2.973	4.352	0.36	0.662	1.718	1.846	1.861
Ru	0.257	0.683	3.122	1.209	0.973	1.726	1.926	1.839
Rh	1.121	2.635	4.05	0.283	0.36	1.823	2.012	2.033
Pd	1.652	3.345	4.921	0.463	1.231	1.791	1.931	2.299
Os	-0.161	-0.296	0.786	2.904	1.391	1.741	1.94	1.778
Ir	0.771	1.805	3.77	0.736	0.459	1.819	2.015	1.985
Pt	2.964	3.283	4.995	1.734	1.305	1.784	1.877	2.322
Ti	-2.599	-2.564	0.72	2.97	3.829	1.632	1.804	1.886
V	-2.741	-2.938	-1.647	5.337	3.971	1.596	1.779	1.611
Cr	-0.39	-0.4	2.791	1.961	1.62	1.568	1.809	1.806
Mn	-0.131	0.149	3.126	1.747	1.361	1.574	1.834	1.846
Cu	1.063	2.987	4.062	0.695	0.372	1.743	1.83	1.855
Zn	0.101	2.682	3.461	1.351	1.129	1.853	1.849	1.911
Au	0.357	6.75	4.817	5.163	3.163	2.158	1.95	2.818
Zr	-3.136	-2.682	0.318	3.372	4.366	1.771	1.934	2.046
Nb	-2.722	-2.971	-3.428	7.118	3.952	1.717	1.894	1.721
Mo	-3.053	-3.507	-0.688	4.378	4.283	1.682	1.877	1.674
Hf	-3.558	-2.834	-0.16	3.85	4.788	1.78	1.912	2.024
Ta	-3.147	-3.302	-3.916	7.606	4.377	1.746	1.895	1.75
W	-3.363	-3.765	-4.114	7.804	4.593	1.719	1.881	1.734
Sc	-3.1	-1.166	0.299	3.391	4.33	1.735	1.868	1.983
Y	-3.376	-1.138	-0.017	3.707	4.606	1.876	2.021	2.14
Cd	-0.051	2.638	3.331	1.459	1.281	2.052	2.055	2.113
Ag	1.448	3.516	4.306	0.837	0.616	1.974	2.058	2.128
Re	-3.727	-4.134	-3.182	6.872	4.957	1.712	1.894	1.745

Table S6. The adsorption Gibbs free energies (eV) and the bond length (Å) of reaction intermediates of OH, O and OOH, overpotentials (V) of OER and ORR on TM@$C_{54}N_4$-pyrid-pyrro..

TM	ΔG_{*OH}	ΔG_{*O}	ΔG_{*OOH}	η_{OER}	η_{ORR}	M-O	M-OH	M-OOH

Fe	0.271	1.268	3.409	0.912	0.959	1.624	1.832	1.742
Co	1.028	2.248	4.069	0.591	0.379	1.646	1.85	1.825
Ni	1.71	3.273	4.802	0.48	1.112	1.698	1.832	1.987
Ru	0.05	0.456	2.783	1.098	1.18	1.711	1.903	1.779
Rh	1.078	2.598	3.952	0.29	0.262	1.779	1.973	1.993
Pd	2.31	4.478	4.979	1.08	1.289	2.021	1.928	2.363
Os	-0.285	-0.182	2.32	1.37	1.515	1.733	1.922	1.768
Ir	0.816	2.016	3.769	0.524	0.414	1.806	1.991	1.968
Pt	2.29	3.982	5.062	1.06	1.372	1.782	2.068	2.391
Ti	-2.07	-2.018	1.287	2.403	3.3	1.634	1.799	1.887
V	-1.328	-1.725	-0.778	4.468	2.558	1.596	1.78	1.603
Cr	-0.157	-0.215	3.006	1.991	1.387	1.565	1.801	1.837
Mn	0.005	0.555	3.146	1.361	1.225	1.571	1.814	1.864
Cu	1.725	3.638	4.658	0.684	0.968	1.738	1.833	1.868
Zn	0.87	3.491	4.034	1.391	0.687	1.864	1.862	1.945
Au	1.648	3.43	4.884	0.552	1.194	1.861	1.966	2.896
Zr	-3.701	-3.297	-0.334	4.024	4.931	1.772	1.931	2.044
Nb	-3.429	-3.768	-4.269	7.959	4.659	1.717	1.887	1.721
Mo	-1.45	-2.182	-1.328	5.018	2.68	1.682	1.858	1.692
Hf	-4.143	-3.446	-2.491	6.181	5.373	1.781	1.908	1.825
Ta	-2.597	-2.791	-3.413	7.103	3.827	1.744	1.886	1.749
W	-1.871	-2.644	-2.408	6.098	3.101	1.718	1.869	1.73
Sc	-1.874	0.631	1.439	2.251	3.104	1.754	1.87	1.987
Y	-3.497	-0.786	-0.192	3.882	4.727	1.905	2.024	2.149
Cd	0.642	3.304	3.9	1.432	0.634	2.074	2.064	2.14
Ag	1.569	3.912	4.383	1.113	0.759	1.92	2.01	2.072
Re	-1.29	-2.215	-0.866	4.556	2.52	1.704	1.886	1.727

Table S7. The adsorption Gibbs free energies (eV) and the bond length (Å) of reaction intermediates of OH, O and OOH, overpotentials (V) of OER and ORR on TM@$C_{64}N_4$-pyrid.

TM	ΔG_{*OH}	ΔG_{*O}	ΔG_{*OOH}	η_{OER}	η_{ORR}	M-O	M-OH	M-OOH

Fe	0.07	1.194	3.302	0.878	1.16	1.638	1.824	1.834
Co	0.813	2.024	3.797	0.543	0.417	1.653	1.863	1.851
Ni	1.32	2.86	4.357	0.309	0.667	1.718	1.848	1.857
Ru	0.22	0.463	3.204	1.511	1.01	1.725	1.938	1.924
Rh	1.027	2.419	4.013	0.364	0.323	1.82	2.022	2.032
Pd	1.543	3.196	4.913	0.487	1.223	1.789	1.926	2.311
Os	-0.273	-0.521	0.542	3.148	1.503	1.742	1.941	1.778
Ir	0.618	1.629	3.657	0.798	0.612	1.819	2.015	1.989
Pt	1.735	2.836	4.72	0.654	1.03	1.768	2.083	2.159
Ti	-2.384	-2.323	-1.773	5.463	3.614	1.633	1.804	1.648
V	-2.816	-2.565	-2.173	5.863	4.046	1.594	1.779	1.609
Cr	-0.424	-0.383	2.753	1.906	1.654	1.571	1.793	1.858
Mn	-0.161	0.151	3.121	1.74	1.391	1.577	1.839	1.851
Cu	0.98	2.909	4.093	0.699	0.403	1.741	1.825	1.857
Zn	0.029	2.595	3.409	1.336	1.201	1.851	1.848	1.906
Au	0.261	2.244	4.803	1.329	1.113	1.868	1.95	2.839
Zr	-2.984	-2.529	0.333	3.357	4.214	1.771	1.938	2.051
Nb	-2.741	-2.919	-3.41	7.1	3.971	1.718	1.895	1.722
Mo	-3.212	-3.518	-3.447	7.137	4.442	1.683	1.881	1.707
Hf	-3.389	-2.657	-0.007	3.697	4.619	1.78	1.915	2.028
Ta	-3.175	-3.257	-3.918	7.608	4.405	1.747	1.893	1.752
W	-3.764	-3.886	-4.471	8.161	4.994	1.721	1.883	1.736
Sc	-3.066	-1.188	0.254	3.436	4.296	1.734	1.869	1.981
Y	-3.464	-1.299	-0.163	3.853	4.694	1.873	2.021	2.141
Cd	-0.104	2.462	3.277	1.336	1.334	2.06	2.055	2.111
Ag	1.391	3.506	4.368	0.885	0.678	1.963	2.048	2.118
Re	-4.056	-4.321	-3.474	7.164	5.286	1.715	1.893	1.748

Table S8. The adsorption Gibbs free energies (eV) and the bond length (Å) of reaction intermediates of OH, O and OOH, overpotentials (V) of OER and ORR on TM@$C_{64}N_4$-pyrid-pyrro.

TM	ΔG_{*OH}	ΔG_{*O}	ΔG_{*OOH}	η_{OER}	η_{ORR}	M-O	M-OH	M-OOH

Fe	0.158	1.171	3.565	1.165	1.072	1.623	1.831	1.787
Co	0.935	2.12	3.967	0.617	0.295	1.644	1.844	1.827
Ni	1.705	3.235	4.8	0.475	1.11	1.696	1.826	1.987
Ru	0.042	0.387	2.726	1.109	1.188	1.711	1.896	1.761
Rh	0.99	2.411	3.854	0.213	0.24	1.777	1.97	1.994
Pd	2.312	4.176	5.013	1.082	1.323	1.777	1.921	2.351
Os	-0.346	-0.306	2.211	1.479	1.576	1.732	1.917	1.76
Ir	0.736	1.912	3.806	0.664	0.494	1.804	1.99	1.974
Pt	2.272	3.971	5.09	1.042	1.4	1.781	2.067	2.385
Ti	-2.149	-2.136	1.207	2.483	3.379	1.633	1.798	1.89
V	-1.43	-1.886	-0.899	4.589	2.66	1.597	1.774	1.604
Cr	-0.19	-0.266	3.005	2.04	1.42	1.565	1.797	1.839
Mn	0.023	0.604	3.151	1.317	1.207	1.569	1.81	1.862
Cu	1.786	3.696	4.719	0.68	1.029	1.737	1.807	1.878
Zn	0.943	3.552	4.048	1.379	0.734	1.867	1.864	1.949
Au	1.566	3.482	4.865	0.686	1.175	1.863	1.966	2.924
Zr	-3.671	-3.304	-2.229	5.919	4.901	1.772	1.928	1.801
Nb	-2.307	-2.549	-2.864	6.554	3.537	1.718	1.883	1.718
Mo	-1.503	-2.267	-1.621	5.311	2.733	1.682	1.857	1.697
Hf	-4.126	-3.437	-2.398	6.088	5.356	1.781	1.908	1.836
Ta	-2.681	-2.869	-3.434	7.124	3.911	1.745	1.885	1.751
W	-1.966	-2.789	-2.589	6.279	3.196	1.718	1.867	1.729
Sc	-1.928	0.641	1.391	2.299	3.158	1.756	1.87	1.987
Y	-1.802	1.01	1.512	2.178	3.032	1.906	2.024	2.15
Cd	0.714	3.265	3.917	1.321	0.578	2.081	2.067	2.155
Ag	1.563	3.915	4.376	1.122	0.769	1.918	2.007	2.07
Re	-1.263	-2.373	-1.161	4.851	2.493	1.704	1.887	1.73

Table S9. NBO, AIM, Bader charges $Q(|e|)$ of TM@$C_{54}N_4$-pyrid, TM@$C_{54}N_4$-pyrro, TM@$C_{64}N_4$-pyrid, and TM@$C_{64}N_4$-pyrro. (TM = Co, Rh, Ir)

TM@$C_{54}N_4$-pyrid	Q ($\|e\|$)

TM	NBO	AIM
Co	0.73961	0.8494
Rh	0.69133	0.7456
Ir	0.79903	0.8521
TM@$C_{54}N_4$-pyrid-pyrro		
Co	0.80358	0.9113
Rh	0.7294	0.7968
Ir	0.79576	0.889
TM@$C_{64}N_4$-pyrid		
Co	0.75299	0.8579
Rh	0.70908	0.7362
Ir	0.81434	0.8786
TM@$C_{64}N_4$-pyrid-pyrro		
Co	0.81085	0.9346
Rh	0.74021	0.8197
Ir	0.79601	0.8988

Table S10. Calculated electron density $\rho(r_c)$ ρ and its Laplacian $\nabla^2\rho(r_c)$ at the bond critical point, bond length, and Wiberg bond orders *P*(TM-N) of TM-N in TM@$C_{54}N_4$-pyrid, TM@$C_{54}N_4$-pyrro, TM@$C_{64}N_4$-pyrid, and TM@$C_{64}N_4$-pyrro. (TM = Co, Rh, Ir)

TM@$C_{54}N_4$-pyrid	$\rho(r_c)$	$\nabla^2\rho(r_c)$	BL	BL(PBE)	*P*(TM-N)
Co-N1	0.123221	0.488037	1.872127	1.869	0.4446
Co-N2	0.123221	0.488037	1.872127	1.869	0.4446
Co-N3	0.123221	0.488037	1.872127	1.868	0.4446
Co-N4	0.123221	0.488037	1.872127	1.868	0.4446
Rh-N1	0.128277	0.427088	1.99	1.984	0.453
Rh-N2	0.128277	0.427088	1.99	1.983	0.453
Rh-N3	0.128277	0.427088	1.99	1.984	0.453
Rh-N4	0.128277	0.427088	1.99	1.985	0.453
Ir-N1	0.146511	0.436251	1.972345	1.978	0.5617
Ir-N2	0.146511	0.436251	1.972345	1.977	0.5617
Ir-N3	0.146511	0.436251	1.972345	1.977	0.5617

Ir-N4	0.146511	0.436251	1.972345	1.977	0.5617
TM@$C_{54}N_4$-pyrid-pyrro					
Co-N1	0.124477	0.46638	1.869603	1.884	0.4336
Co-N2	0.122102	0.456943	1.876957	1.883	0.457
Co-N3	0.122102	0.456943	1.876957	1.883	0.457
Co-N4	0.124477	0.46638	1.869603	1.885	0.4336
Rh-N1	0.129295	0.408308	1.988829	1.99	0.4514
Rh-N2	0.12798	0.404772	1.991095	1.994	0.4811
Rh-N3	0.12798	0.404772	1.991095	1.993	0.4811
Rh-N4	0.129295	0.408308	1.988829	1.99	0.4514
Ir-N1	0.143769	0.415027	1.981557	1.985	0.5362
Ir-N2	0.141329	0.417274	1.985292	1.986	0.5572
Ir-N3	0.141329	0.417274	1.985292	1.986	0.5572
Ir-N4	0.143769	0.415027	1.981557	1.986	0.5362
TM@$C_{64}N_4$-pyrid					
Co-N1	0.126272	0.491744	1.863617	1.86	0.4723
Co-N2	0.119905	0.473963	1.883336	1.873	0.429
Co-N3	0.119905	0.473963	1.883336	1.873	0.429
Co-N4	0.126272	0.491744	1.863617	1.859	0.4723
Rh-N1	0.130014	0.430796	1.985649	1.978	0.4719
Rh-N2	0.126026	0.417219	1.998573	1.991	0.4398
Rh-N3	0.126026	0.417219	1.998573	1.99	0.4398
Rh-N4	0.130014	0.430796	1.985649	1.978	0.4719
Ir-N1	0.147909	0.432521	1.969918	1.972	0.5654
Ir-N2	0.146904	0.432688	1.972042	1.979	0.5692
Ir-N3	0.146904	0.432688	1.972042	1.979	0.5692
Ir-N4	0.147909	0.432521	1.969918	1.971	0.5654
TM@$C_{64}N_4$-pyrid-pyrro					
Co-N1	0.123168	0.456362	1.874369	1.889	0.4274
Co-N2	0.122764	0.453141	1.875359	1.885	0.4604
Co-N3	0.122764	0.453141	1.875359	1.884	0.4604

Co-N4	0.123168	0.456362	1.874369	1.888	0.4274
Rh-N1	0.126389	0.405666	1.995764	1.999	0.446
Rh-N2	0.126968	0.406332	1.99166	1.994	0.4849
Rh-N3	0.126969	0.406332	1.99166	1.994	0.4849
Rh-N4	0.126369	0.405666	1.995764	1.999	0.446
Ir-N1	0.142552	0.408992	1.985844	1.993	0.5319
Ir-N2	0.141493	0.41444	1.985326	1.989	0.5587
Ir-N3	0.141493	0.41444	1.985326	1.989	0.5587
Ir-N4	0.142552	0.408992	1.985844	1.993	0.5319

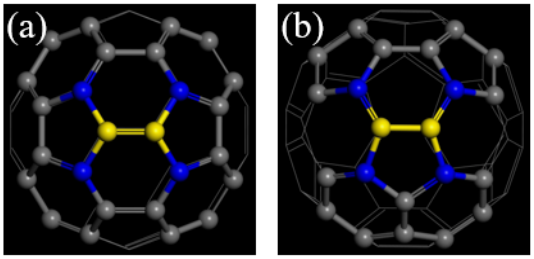

Fig. S1 Construction of the structures and relative energyies for $C_{54}N_4$ computed in the PBE level of theory.

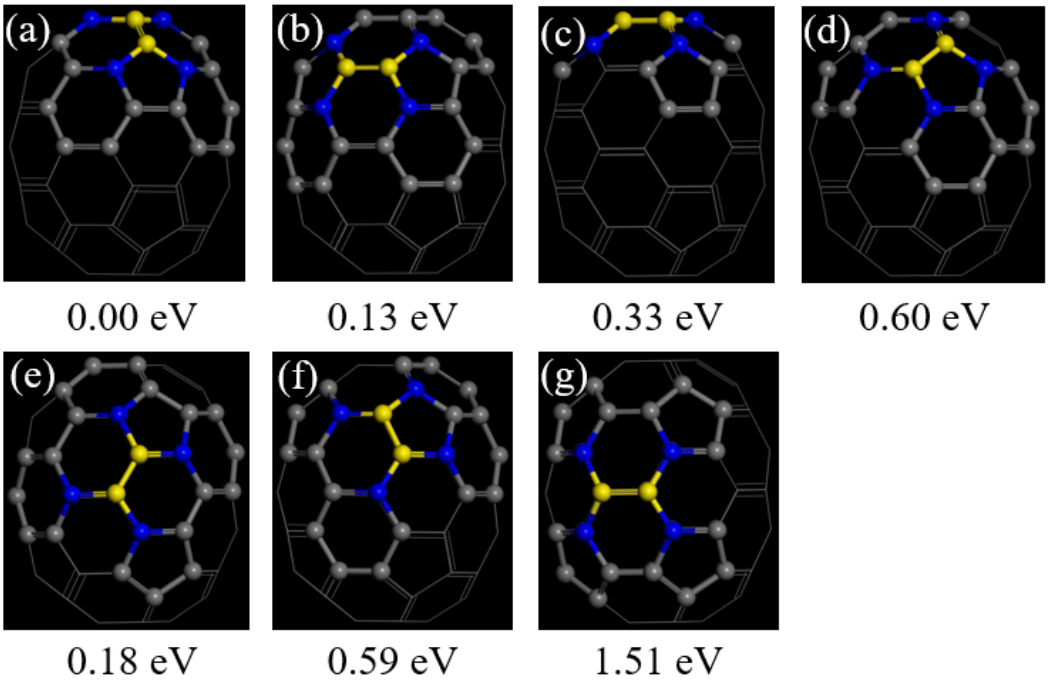

Fig. S2 Construction of the structures and relative energyies for $C_{64}N_4$ computed in the PBE level of theory.

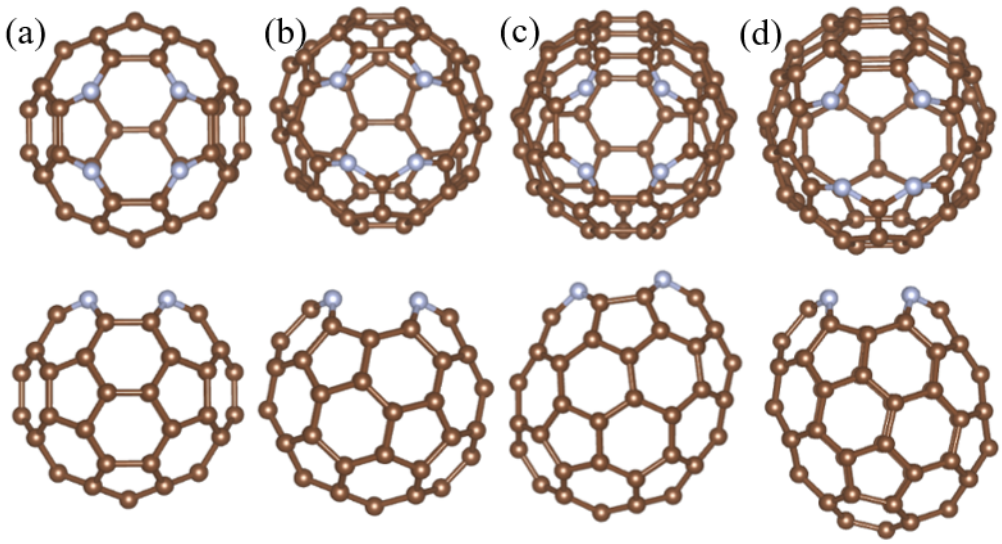

Fig. S3 Top view and side view of (a) $C_{54}N_4$-pyrid with four pyridinic nitrogen, (b) $C_{54}N_4$-pyrid-pyrro with two pyridinic nitrogen and two pyrrolic nitrogen, (c) $C_{64}N_4$-pyrid with four pyridinic nitrogen, (d) $C_{64}N_4$-pyrid-pyrro with two pyridinic nitrogen and two pyrrolic nitrogen.

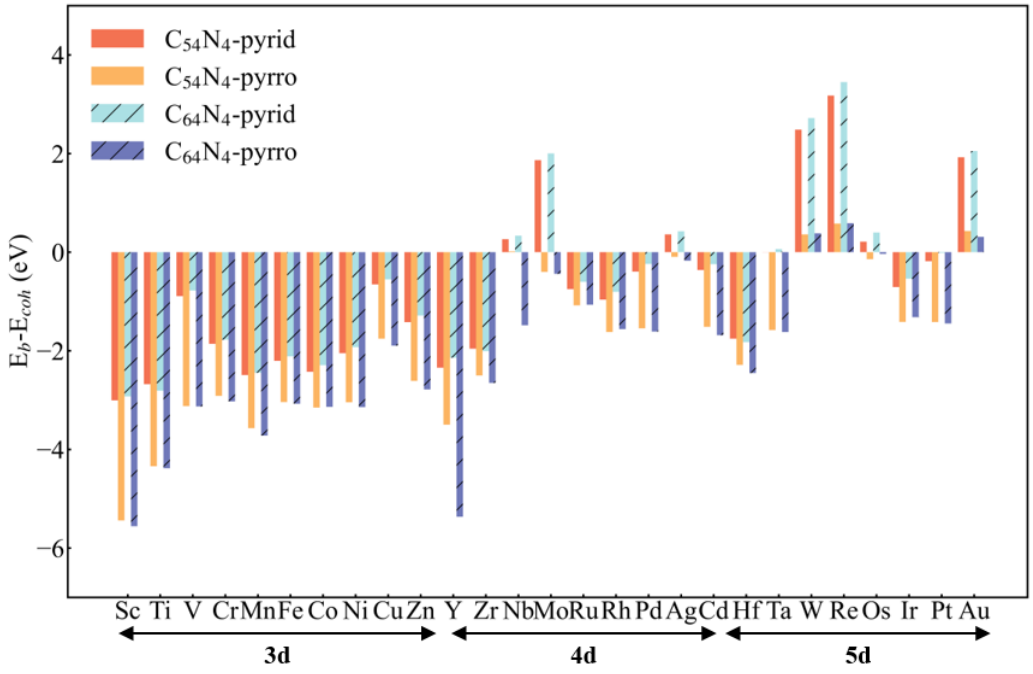

Fig. S4 The differenece between the binding energies of the TM atoms supported on the four azafullerenes $C_{54}N_4$-pyrid (light red bars), $C_{54}N_4$-pyrid-pyrro (orange bars), $C_{64}N_4$-pyrid (light blue bars with diagonal stripes) and $C_{64}N_4$-pyrid-pyrro (dark blue bars with diagonal stripes), and the corresponding cohesive energies.

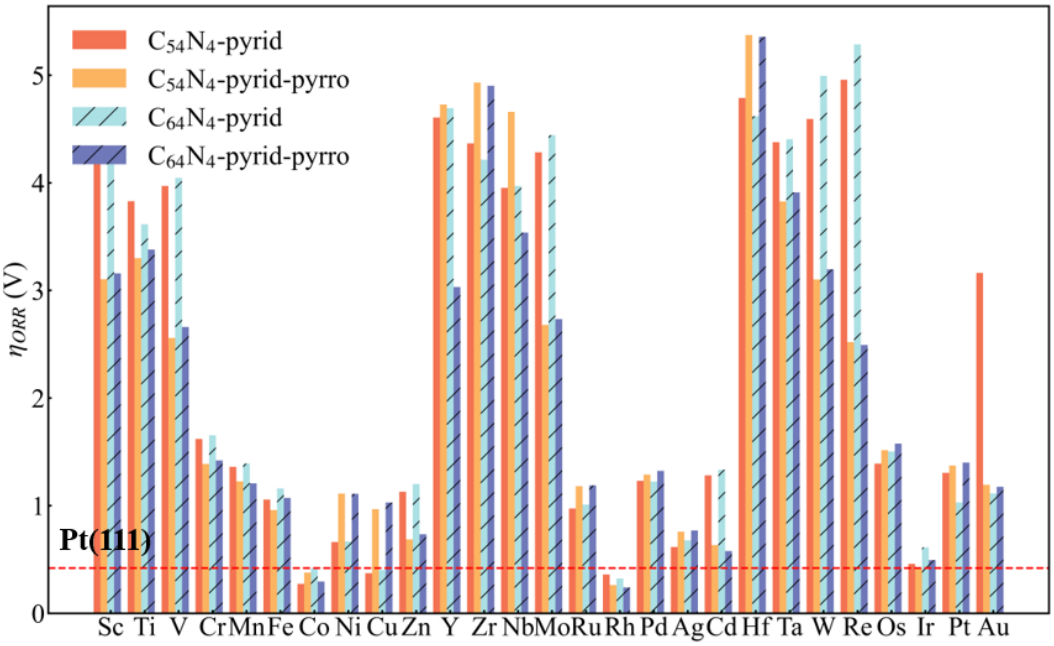

Fig. S5 Summary of the ORR overpotential for TM supported on the four azafullerenes $C_{54}N_4$-pyrid (light red bars), $C_{54}N_4$-pyrid-pyrro (orange bars), $C_{64}N_4$-pyrid (light blue bars with diagonal stripes) and $C_{64}N_4$-pyrid-pyrro (dark blue bars with diagonal stripes).

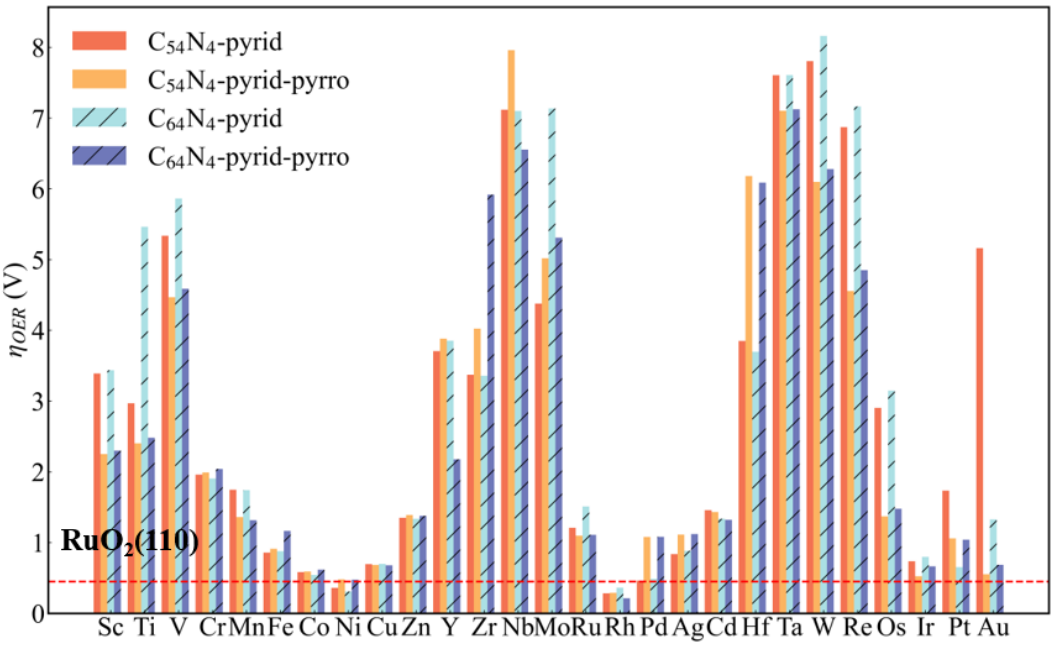

Fig. S6 Summary of the OER overpotential for TM supported on the four azafullerenes $C_{54}N_4$-pyrid (light red bars), $C_{54}N_4$-pyrid-pyrro (orange bars), $C_{64}N_4$-pyrid (light blue bars with diagonal stripes) and $C_{64}N_4$-pyrid-pyrro (dark blue bars with diagonal stripes).

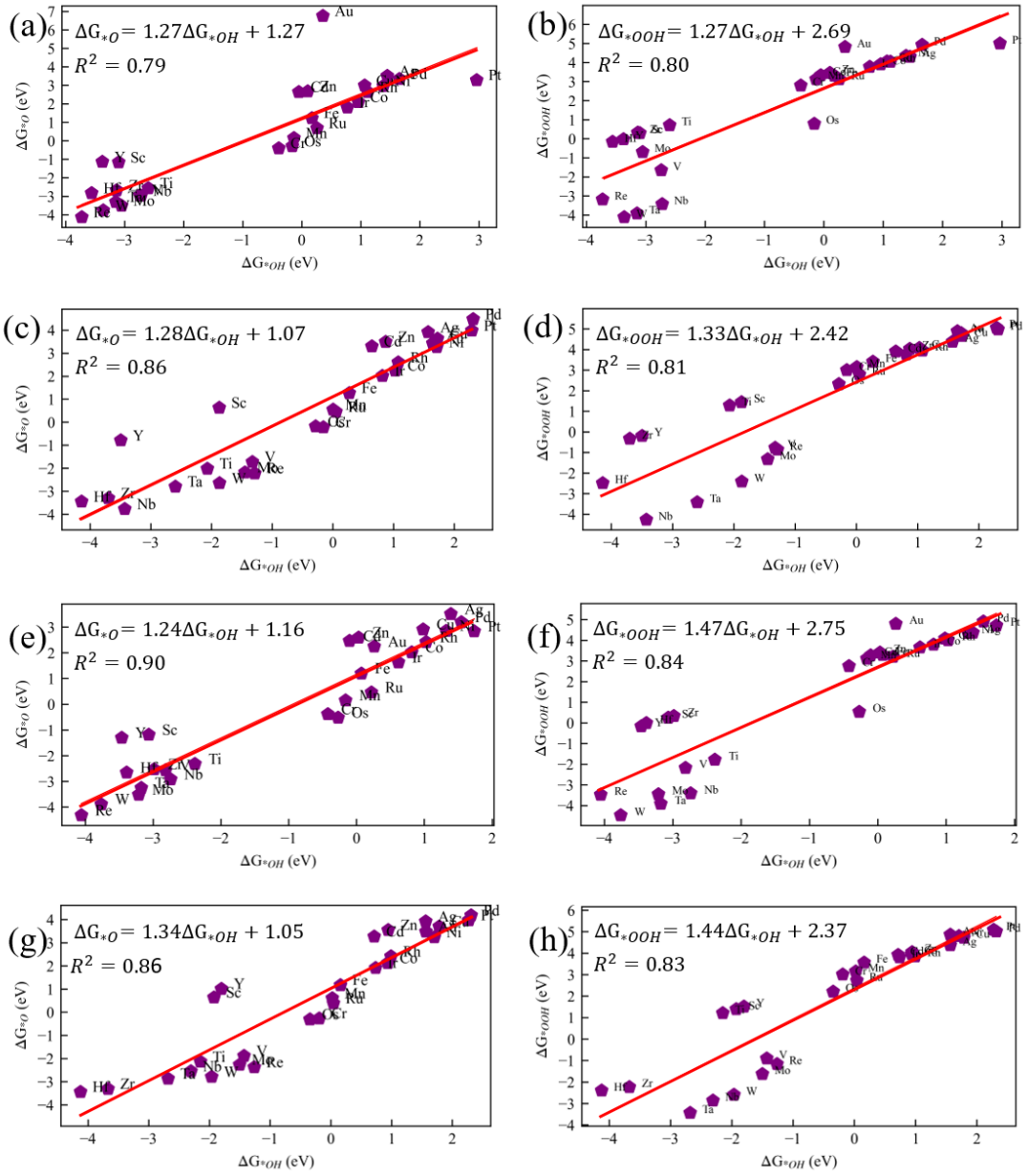

Fig. S7 Scaling relationship between ΔG_{*O} and ΔG_{*OH} for (a) TM@$C_{54}N_4$-pyrid, (c) TM@$C_{54}N_4$-pyrid-pyrro, (e) TM@$C_{64}N_4$-pyrid and (g) TM@$C_{64}N_4$-pyrid-pyrro. And the scaling relationship between ΔG_{*OOH} and ΔG_{*OH} for (b) TM@$C_{54}N_4$-pyrid, (d) TM@$C_{54}N_4$-pyrid-pyrro, (f) TM@$C_{64}N_4$-pyrid and (h) TM@$C_{64}N_4$-pyrid-pyrro.

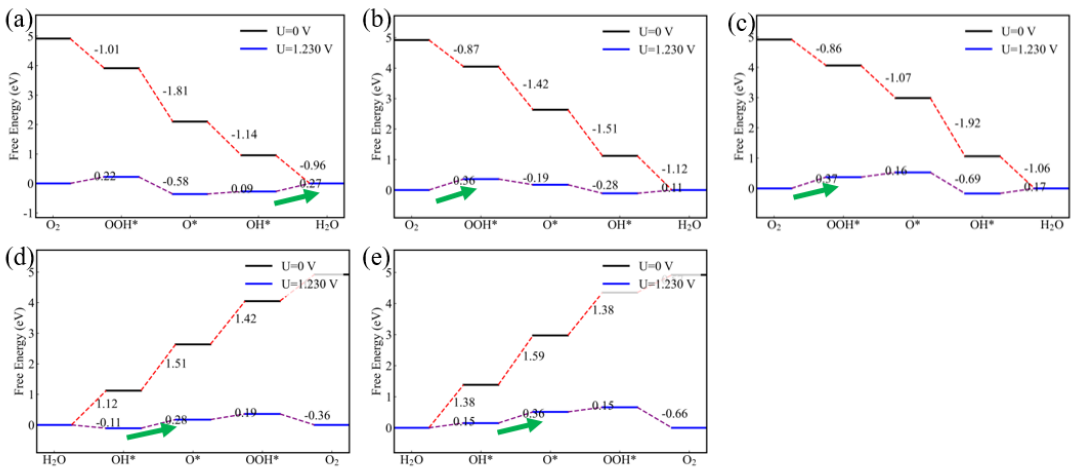

Fig. S8 Adsorption free energies on (a) Co@$C_{54}N_4$-pyrid, (b) Rh@$C_{54}N_4$-pyrid, and (c) Cu@$C_{54}N_4$-pyrid at electrode potentials of 0 and 1.23 V for ORR and on (d) Rh@$C_{54}N_4$-pyrid and (e) Ni@$C_{54}N_4$-pyrid at 0 and 1.23 V for OER.

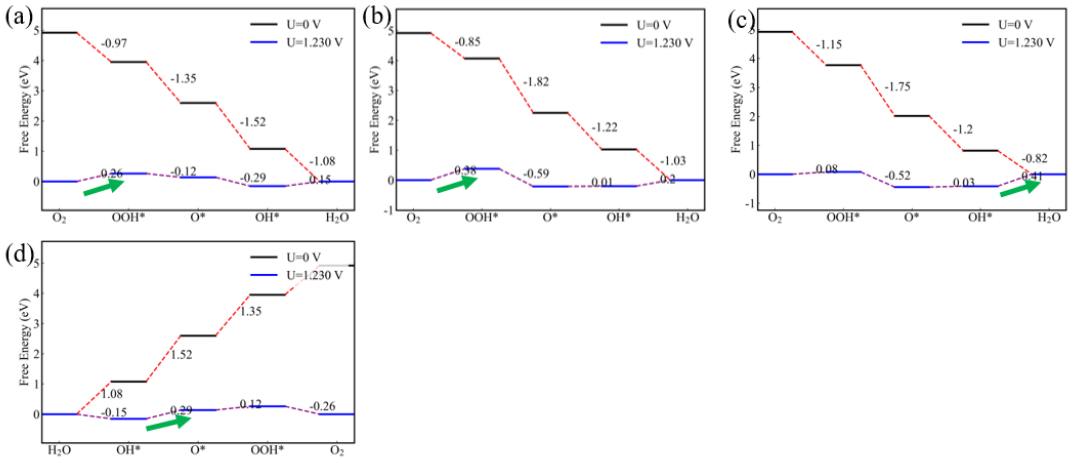

Fig. S9 Adsorption free energies on (a) Rh@$C_{54}N_4$-pyrid-pyrro, (b) Co@$C_{54}N_4$-pyrid-pyrro, and (c) Ir@$C_{54}N_4$-pyrid-pyrro at electrode potentials of 0 and 1.23 V for ORR and on (d) Rh@$C_{54}N_4$-pyrid-pyrro at 0 and 1.23 V for OER.

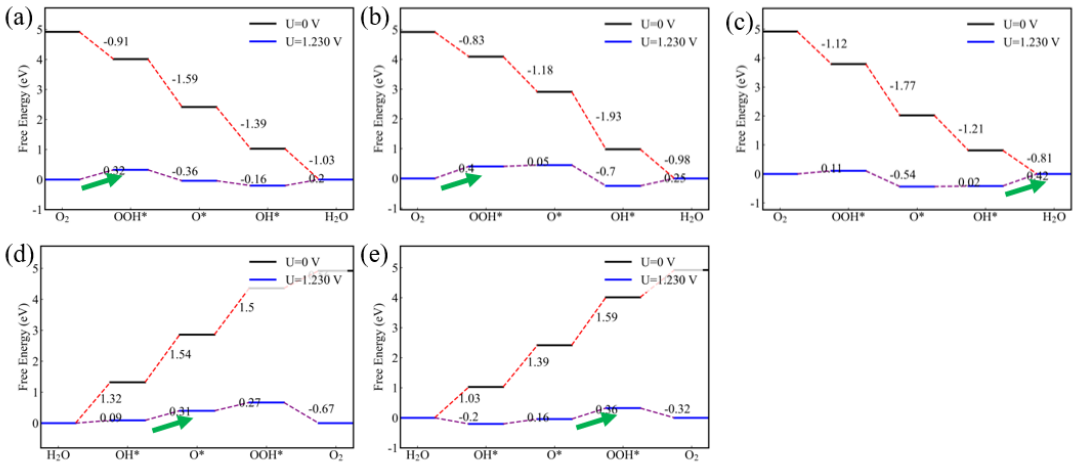

Fig. S10 Adsorption free energies on (a) Rh@$C_{64}N_4$-pyrid, (b) Cu@$C_{64}N_4$-pyrid, and (c) Co@$C_{64}N_4$-pyrid at electrode potentials of 0 and 1.23 V for ORR and on (d) Ni@$C_{64}N_4$-pyrid and (e) Rh@$C_{64}N_4$-pyrid at 0 and 1.23 V for OER.

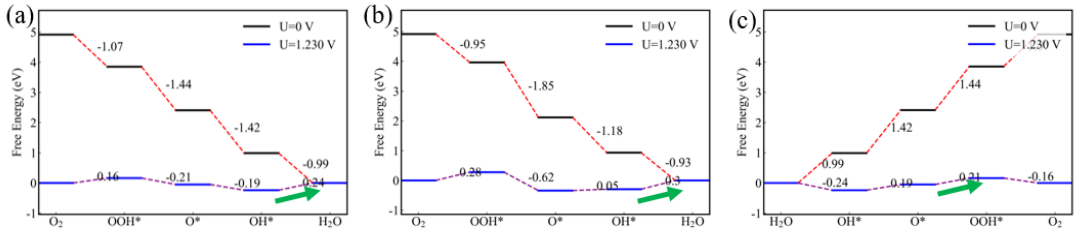

Fig. S11 Adsorption free energies on (a) Rh@$C_{64}N_4$-pyrid-pyrro and (b) Co@$C_{64}N_4$-pyrid-pyrro at electrode potentials of 0 and 1.23 V for ORR and on (c) Rh@$C_{64}N_4$-pyrid-pyrro at 0 and 1.23 V for OER.

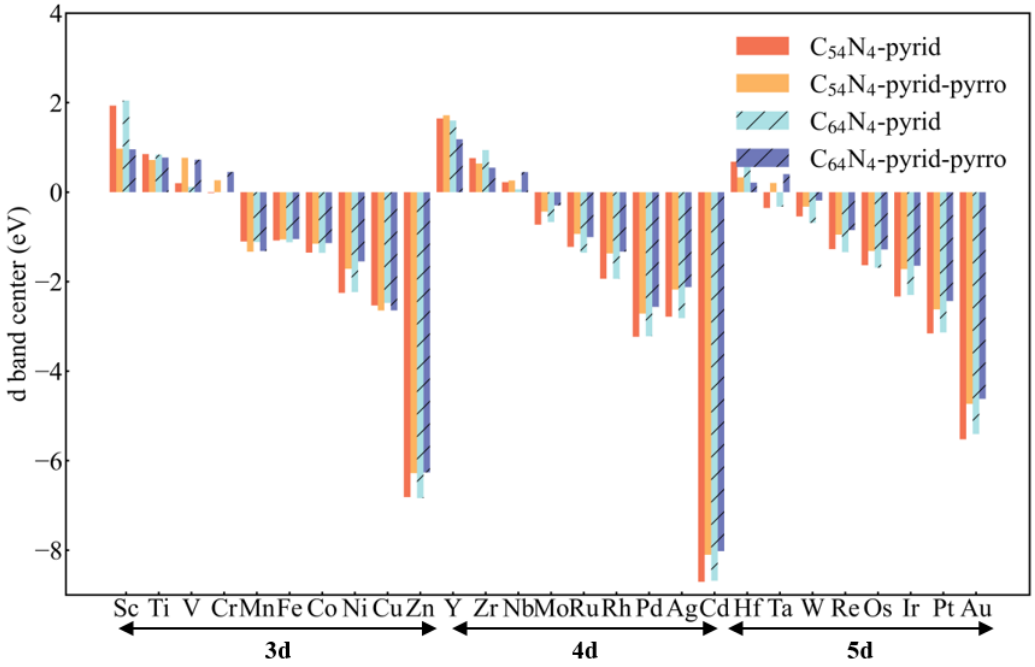

Fig. S12 *d*-band center energies of the TM atoms on $C_{54}N_4$- pyrid, $C_{54}N_4$-pyrid-pyrro, $C_{64}N_4$- pyrid and $C_{54}N_4$-pyrid-pyrro.

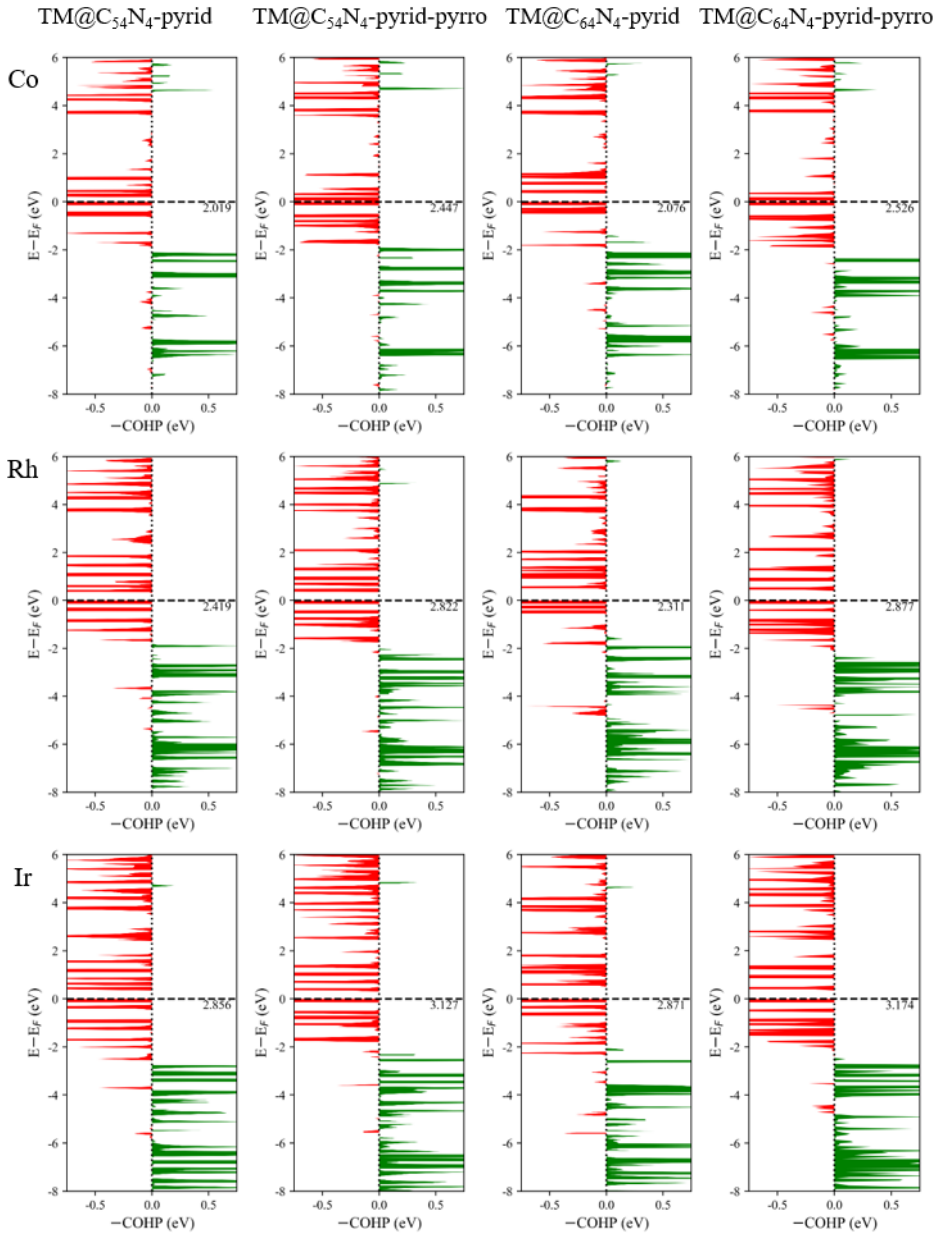

Fig. S13 Crystal orbital Hamilton population (COHP) between the active centers TM and the OH* intermediate for TM@$C_{54}N_4$-pyrid, TM@$C_{54}N_4$-pyrid-pyrro, TM@$C_{64}N_4$-pyrid TM@$C_{64}N_4$-pyrid-pyrro with the bonding state (green) and antibonding (red) state. (TM = Co, Rh, and Ir).

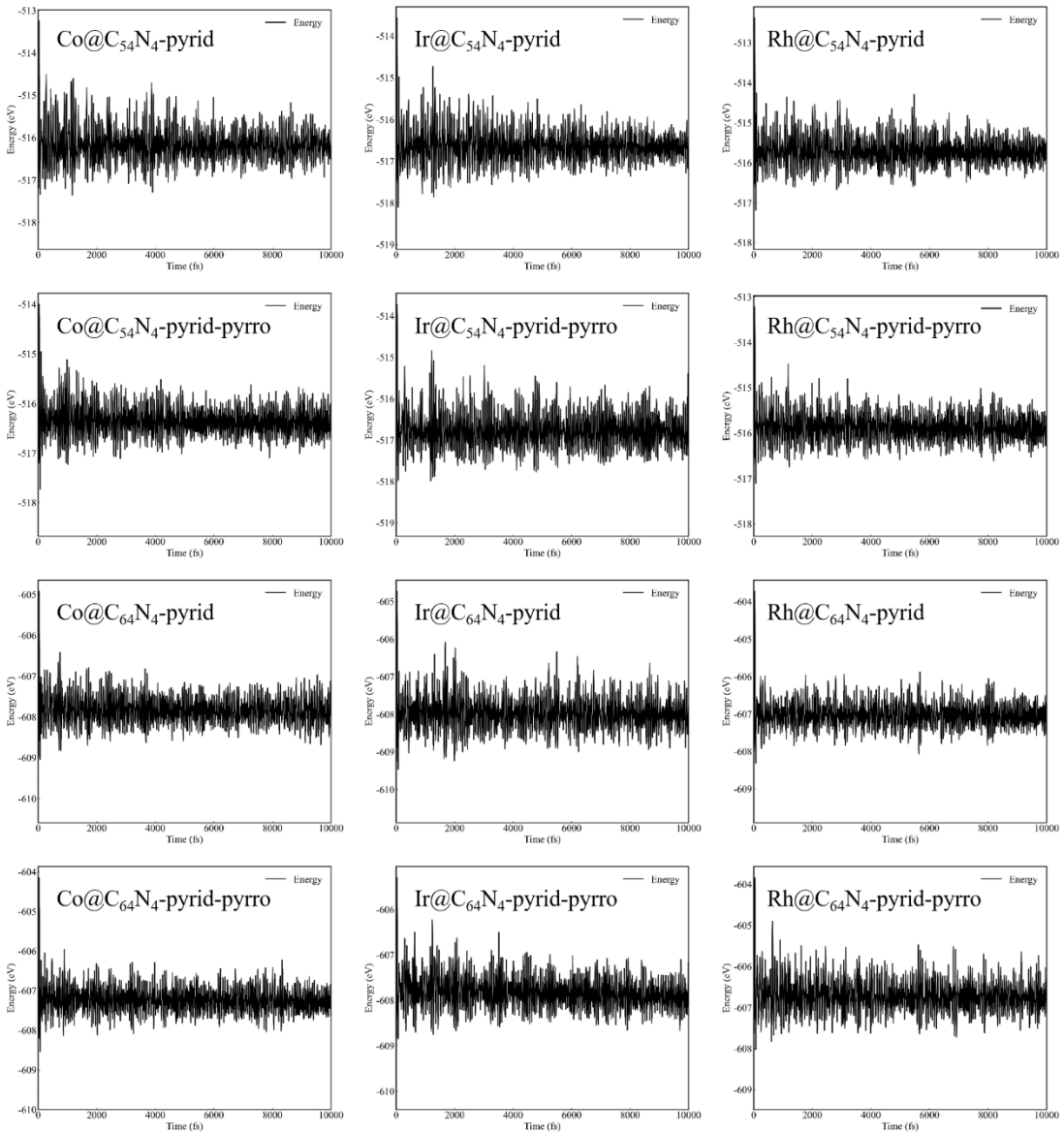

Fig. S14 Evolution of the temperature and the total energy within 10 ps AIMD simulations at 300 K for TM@$C_{54}N_4$-pyrid, TM@$C_{54}N_4$-pyrid-pyrro, TM@$C_{64}N_4$-pyrid, and TM@$C_{64}N_4$-pyrid-pyrro (TM = Co, Rh, Ir).

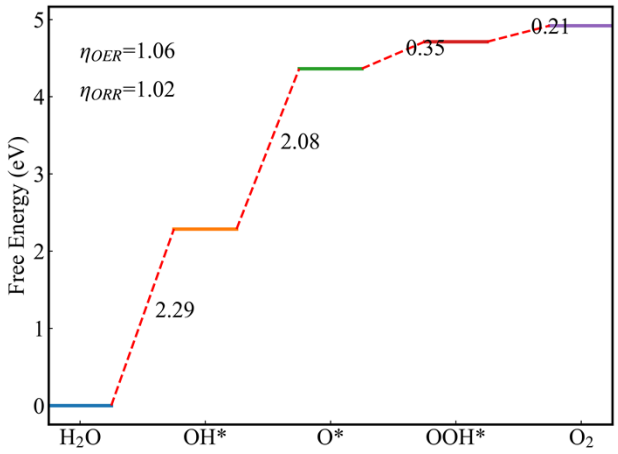

Fig. S15 Adsorption free energies on PtN_4@graphene.

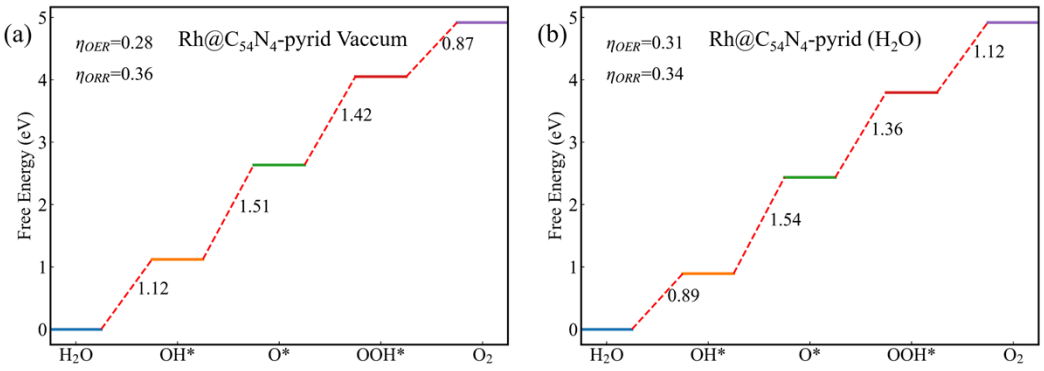

Fig. S16 A comparison of adsorption free energies on $Rh@C_{64}N_4$-pyrid from the vaccum and implicit solvent (H_2O) model.