Ultralow Non-Noble Metal loaded MOF Derived Bi-Functional Electrocatalysts for Oxygen Evolution and Reduction Reactions

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Figure S20. ORR polarization curve at different rotating speeds for (a) MOF1, (c) 23 MOF2 (e) MOF3; ORR stability plot of taking linear sweep voltammogram after a different number of potential cycles have been plotted for (b) MOF1, (d) MOF2 (f) MOF3. ORR voltammograms of MOF catalysts were recorded at a rotation rate of 1600 rpm in O₂ saturated 0.1 M KOH using RDE.

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Experimental Details

1.1 Synthesis

5-[(Anthracen-9-ylmethyl)-amino]-isophthalic Acid (H₂L): 9- Anthracene carboxaldehyde (1.031 g, 5 mmol) was slowly added to a stirred solution of 5-aminoisophthalic acid (0.905 g, 5 mmol) in 50 mL of dry methanol and refluxed for one and half hour. After cooling the reaction mixture, NaBH₄ was slowly added to the reaction mixture at 4 °C. The solvent was removed under vacuum. The residue was dissolved in 50 mL of water and treated with acetic acid to make pH 5-6. The product came out as a pale-yellow colored precipitate, which is collected, washed thoroughly with water, and air-dried after filtration. Yield: 1.527g (77%). ¹H-NMR: (DMSO-d₆) 400 MHz, δ): 11.49 (s, 1H), 8.65 (s, 1H), 8.30 (d, 8Hz, 2H), 8.14 (d, 4Hz, 2H), 7.79 (s, 1H), 7.61 (m, 2H), 7.56 (m, 4H), 6.51 (s, 1H), 5.14 (s, 2H). ¹³C-NMR: (DMSO-d₆, 100 MHz, δ): 167.7, 149.4, 132.4, 131.1, 130.2, 129.5, 129.4, 126.4, 125.8, 125.2, 117.8, 116.3, 103.3, 55.8; ESI-

MS: m/z [M–1]: 370.2734 (100%). IR (cm⁻¹): 3398(s), 2877 (m), 1686 (s), 1600 (s), 1503 (s), 1436 (s), 1272 (s), 949 (m), 893 (m), 728 (s).

{[Co₄(L)₄(py)₈]*.py*}_n (MOF1). A solid mixture of ligand H₂L (18.5 mg, 0.05 mmol) and CoCl₂.6H₂O (23.7 mg, 0.1 mmol) was taken together in a mixture of 25 mL DMF/pyridine (2:1 V/V) and stirred for half an hour. The contents were transferred into a Teflon-lined steel autoclave and heated at 100 °C for 48 hours under autogenous pressure, then allowed to cool to room temperature at the rate of 1 °C/min. Red-colored crystals of **MOF1** were collected, washed with water, and air-dried. Yield: 60%, FT-IR (cm⁻¹): 3061 (w), 1589 (w), 1446 (s), 1387 (s), 1215 (m), 1039 (m), 727 (s), 696 (s), 628 (m).

{[Co(L)(H₂O)phen]}_n (MOF2). By employing the chelating linker 1,10-phenanthroline (phen) as a co-ligand MOF2 was synthesized. To the reaction mixture CoCl₂.5H₂O (23.8 mg, 0.1 mmol), ligand H₂L (27.7 mg, 0.08 mmol) in 20 mL of DMF/water (2:1 V/V), 1,10-phenanthroline (11.4 mg, 0.06 mmol) was added and sealed in a 25 mL vial. The mixture was heated to 100° C for 48 hours under autogenous pressure and then allowed to cool to room temperature. Red-colored crystals of MOF2 were collected from the mixture, washed with water, and air-dried to obtain 70 % yield based on Co. FT-IR (cm⁻¹): 3240 (w), 1597 (s), 1355 (s), 1099 (m), 950 (m), 774 (s), 715 (s), 528 (m), 444 (m).

{[Co(aip)(H₂O)].2H₂O}_n (MOF3). CoCl₂.6H₂O (37.1 mg, 0.1 mmol), aip (18.1 mg, 0.1 mmol) and 20 mL of DMF/water (2:1 V/V) were sealed together in a Teflon lined autoclave and heated to 100° C for 48 hours. The reaction vessel was cooled to room temperature at the rate of 1 °C/min to obtain yellow-colored crystals of MOF3, which were collected, dried, and washed with water. Yield 65% based on Co. FTIR (cm⁻¹): 3062 (w), 1540 (s), 1423 (s), 1369 (s), 1276 (m), 1193 (m), 848 (s), 780 (s), 726 (s).

1.2 Characterization Techniques

Single crystal X-ray diffraction: Single-crystal X-ray diffraction measurements were performed on Bruker-Apex Duo diffractometer with I μ S microfocus using MoK α radiation. Measurements were carried out at 110(2) K on crystals coated with a thin layer of amorphous oil. The structures were solved by direct and Fourier methods and refined by full-matrix least-squares, using standard crystallographic software: SHELXT-2014, SHELXL- 2014.^{1, 2} The integrity of the crystalline products **1-3** was confirmed in each case by repeated measurements of

the unit-cell dimensions from different single crystallites, as well as by matching between the simulated and experimental powder X-ray diffraction patterns.

Powder X-ray diffraction: Power XRD measurements were done at room temperature on a Rigaku Miniflex X-ray diffractometer with Cu-K_a X-ray source ($\lambda = 1.5406$ Å), equipped with a position-sensitive detector in the angular range $20^{\circ} \le 2\theta \le 80^{\circ}$ with the step size 0.02° and scan rate of 0.5 s/step calibrated against corundum standards. The experimental XRD patterns were compared to the pattern simulated from the data reported in the literature.

IR Spectroscopy: The IR spectra were recorded in ATR mode at room temperature on a Bruker IFS 66v/S spectrophotometer IR spectrophotometer. The symmetric and asymmetric stretching frequencies of the coordinated carboxylate groups appeared around 1355 to 1597 cm⁻¹. The bands aroused due to solvent molecules are observed in the region around 3300 cm⁻¹.

Transmission electron microscopy (TEM): TEM and high-resolution TEM images, selected area electron diffraction (SAED) patterns were collected using a JEOL 200 TEM instrument. Samples for these measurements were prepared by dropping a small volume of sonicated nanocrystalline powders in ethanol onto a carbon-coated copper grid.

Aberration corrected FEI Titan G2 60 kV– 300 kV microscope has been used to investigate the nature of single-atom catalyst. High-Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF STEM) imaging and X-ray Energy Dispersive Spectroscopy (XEDS) have been performed at an accelerating voltage of 300 kV with a probe convergence angle of 24.5 mrad using 70 μ m aperture.

Field Emission Scanning Electron Microscopy (FESEM): FESEM and Quantitative microanalysis on all the samples were performed with an FEI NOVA NANO SEM 600 instrument equipped with an EDAX[®] instrument. Data were acquired with an accelerating voltage of 15 kV. The Energy-dispersive X-ray spectroscopy (EDS) analysis was performed using P/B-ZAF standardless method (where Z = atomic number correction factor, A = absorption correction factor, F = fluorescence factor, P/B = peak to background model) on selected spots and points.

Because of the juxtaposition of the peak positions of EDS energy corresponding to carbon and nitrogen, the height and width of the carbon peak (K α , 0.277), which is located in the vicinity of the nitrogen peak (K α , 0.392), did not allow the nitrogen content of the catalysts to be quantified

accurately. As in our catalysts, N content is extremely low compared to carbon, and it is very difficult to get exact information about the percentage of N present in the catalyst.

Thermogravimetric analysis (TGA): Thermal stability of the MOFs was studied from TGA curves which are recorded under N_2 flow from room temperature to 600-700 °C. **MOF1** exhibits thermal stability up to 400 °C with weight loss of 1.45 % (theoretical weight loss 1.34 %) corresponding to solvent pyridine, which was then undergoing continuous decomposition attributed to the coordinated py, and organic part of the linker. **MOF2** shows weight losses of 6 % (theoretical weight loss 5.08%) equivalent to the lattice and coordinated water molecules up to 150 °C, and a Sharp weight loss 48% (theoretical weight loss of 48.77 was observed in the region 330- 450 °C, which can be the decomposition of the linker. **MOF3** undergoes initial weight loss of 10% (theoretical weight loss 10.03%) up to 180 °C related to coordinated and guest water molecules. The residual compound undergoes gradual weight loss of the organic linker. All three MOFs display thermal stability up to 350 °C and undergo continuous decomposition of organic linkers to gives the residue of metal oxides.

X-ray absorption spectroscopy (XAS): X-ray absorption spectroscopy (XAS) measurements of Co k-edge were carried out at the P64 beamline PETRA, DESY synchrotron source in Germany. The beamline optics mainly consists of an Rh/Pt coated collimating meridional cylindrical mirror and Si (111) double crystal monochromator (DCM). Pellets for the measurements were made by homogeneously mixing the sample with an inert cellulose matrix to have an X-ray absorption edge jump close to one. A standard data analysis procedure was used to extract the EXAFS signal from the measured absorption spectra. Background subtraction, normalization, and alignment of the EXAFS data were performed by using the ATHENA software. EXAFS data of the catalyst materials were Fourier transformed in the range of 4–13.8 Å⁻¹. It was then plotted in R space and analyzed.

X-ray photoelectron spectroscopy (XPS): XPS measurements were carried out using Thermo K-alpha⁺ spectrometer using micro-focused and monochromated Al K α radiation with energy 1486.6 eV. The pass energy for the spectral acquisition was kept at 50 eV for individual corelevels. The electron flood gun was utilized for providing charge compensation during data acquisition. Further, the individual core-level spectra were checked for charging using C1s at 284.8 eV as standard and corrected if needed. The peak fitting of the individual core-levels was done using XPSpeak 41 software with a Shirley-type background. Atomic Force Microscopy (AFM): A Bruker, Forevision (MMV 1045901 model) instruments microscope in tapping mode with 10 nm diameter containing antimony doped Silicon tip was used to carry out AFM studies. The sample was coated on a Si wafer to perform the study.

Raman Spectroscopy: Raman experiments were performed in backscattering geometry (180°) using a commercial Raman spectrometer [LabRam HR evolution (Horiba)] *equipped with a* solid-state frequency-doubled 532 nm CW Nd-YAG laser and 800 mm focal length monochromator. The room temperature Raman spectra were collected with a laser power of less than 0.5 mW at the sample.

Surface area measurement: Specific surface area measurements were performed on BELSORP-MR6 by adsorption of nitrogen gas at – 77K, applying the Brunauer-Emmett-Teller (BET) calculation. Prior to adsorption analysis, the samples were degassed at 85 °C for 12h. Pore size distributions were derived from desorption isotherms using Barrett-Joyner-Halenda (BJH) method.

1.3 Electrochemical Studies: Electrochemical ORR and OER activity of all the catalysts have been investigated with CHI760E electrochemical workstation in a conventional three-electrode cell configuration. The catalyst inks were prepared by taking 1 mg catalyst dispersed in 200 µL EtOH/H₂O (1:1, v/v %) to form a homogeneous ink by ultrasonication for 2 h. Subsequently, 5 μ L of catalyst ink was dropped on the glassy carbon electrode, and then 5 μ L of Nafion (1 wt %) was added on top of the loaded catalyst. The glassy carbon electrode was polished with 3 and 0.05 µm alumina powder and washed with distilled water. The electrochemical tests of ORR and OER were carried out using that three-electrode cell system with catalyst. A graphite rod was used as the counter electrode, and Hg/HgO was acted as the reference electrode. The electrolyte was used as 0.1 M KOH and 0.5 M KOH for ORR and OER, respectively. In the case of ORR, rotating disc electrode (RDE) experiments were performed, keeping other requirements the same. The calibration of Hg/HgO was performed in the high purity hydrogen saturated 0.1 M KOH with a Pt wire as the working electrode, and the cyclic voltammetry (CV) was conducted at a scan rate of 5 mV/s, and the average of the two potentials at which the current crossed zero was taken to be the thermodynamic potential for the hydrogen electrode reactions. All the overpotential values measured were calibrated with reference to a reversible hydrogen electrode

(RHE). The calibration was conducted in the H₂-saturated 0.1 M KOH with a Pt wire as the working electrode. The linear sweep voltammetry (LSV) was recorded at a scan rate of 5 mV/s with varying rotating speeds from 100 rpm and 3600 rpm. Accelerated degradation test (ADT) was performed with graphite rod (purity > 99.9%, Sigma-Aldrich) to avoid Pt dissolution. Stability tests were carried out at a scan rate of 100 mV s⁻¹ and within a potential window of 0.4–0.9 V vs. RHE. The potential window for the stability test was selected on the basis of previous literature. Selectivity toward H₂O was checked using rotating ring disk electrode (RRDE) where ring as platinum and disk as glassy carbon with 4 mm diameter and keeping all other experimental conditions similar, Pt wire as the counter electrode and Hg/HgO as the reference electrode. RDE was carried out from 0.2 to 1.0 V (vs. RHE) at a rotation rate ranging from 100 to 3600 rpm in O₂ saturated 0.1 M KOH. In the RRDE experiment, the percentage of H₂O₂ produced (*X*_{H2O2}) and the corresponding electron transfer numbers during ORR (*n*) can be determined from the following equations, respectively:

$$X_{H_2O_2}(\%) = \frac{\frac{200I_R}{N}}{I_D + \frac{I_R}{N}}$$

where $I_{\rm R}$ is the ring current, $I_{\rm D}$ is the disk current, and N is the collection efficiency.

1.3.1 Estimation of effective electrode surface area. It is very well-known in the electrochemistry community that cyclic voltammetry (CV) can be used to determine the electrochemical double-layer capacitance of different samples at non-Faradaic overpotentials for estimating the effective electrode surface areas. For that, a series of CV measurements were performed at various scan rates (**10, 20, 30, 50, 80, 100 mV s**⁻¹) between 1.05 V to 1.25 V vs. RHE region, and the sweep segments of the measurements were set to 6 to ensure consistency. A linear trend was obtained from the plot of the difference of current density (ΔJ) in the anodic and cathodic sweeps ($J_{anodic} - J_{cathodic}$) at 1.15 V vs. RHE against the scan rate. The slope of the fitting line is equal to twice the geometric double-layer capacitance (C_{dl}), which is proportional to the effective electrode surface area of the materials. Therefore, the electrochemical surface areas of different samples can be compared with one another based on their C_{dl} values keeping other experimental condition the same for each case

Tables

Parameters	MOF1	MOF2	MOF3
CCDC No.	2003336	2003337	2003338
Empirical formula	C ₁₃₇ H ₁₀₅ Co ₄ N ₁₃ O ₁₆	C ₃₅ H ₂₅ CoN ₃ O ₅	C ₈ H ₁₁ CoNO ₇
Formula weight	2425.05	626.51	292.11
Crystal system	triclinic	monoclinic	triclinic
Space group	РГ	P2 ₁ /c	PT
<i>a</i> , Å	17.5982(7)	18.7708(19)	7.7473(4)
b, Å	18.1494(7)	10.5359(10)	8.5583(5)
<i>c</i> , Å	20.1487(6)	15.8548(17)	8.5836(4)
a (deg)	72.754(2)	90	85.668(4)
β (deg)	85.861(2)	104.370(3)	65.804(3)
γ (deg)	65.030(2)	90	75.899(4)
V, Å	5561.2(4)	3037.5(5)	503.29(5)
Ζ	2	4	2
ρ calc g/cm ³	1.448	1.370	1.928
μ , mm ⁻¹	0.664	0.612	1.731
F(000)	2508	1292	298
Refl collected	64489	42409	10026
Independent refl	14392	3271	2530
GOF	1.047	0.953	1.055
final R indices	R1 = 0.0835	R1 = 0.0348	R1 = 0.0609
[1~20(1)]	wR2 = 0.2225	wR2 = 0.1002	wR2 = 0.1618
R indices (all data)	R1 = 0.1585	R1 = 0.0447	R1 = 0.0688 wR2 = 0.1700
	wR2 = 0.2791	1 $wR2 = 0.1178$	
Completeness (%)	99.5	99.4	99.2

 Table S1. Crystal data and structure refinement parameters for all three MOFs.

Sl.	Catalyst	Mass	Electrolyte	Onset	E _{1/2}	Electron	Ref
No.		Loading		Potential (vs.		transfer	
				RHE)		number	
1.	MOF2	0.354	0.1 M KOH	0.838 V	0.702 V	3.85	This work
2.	MOF2_A	0.354	0.1 M KOH	0.82 V	0.782 V	3.9	This work
3.	Co-N/CNFs	0.6	0.1 M HClO ₄	0.82 V	0.70 V	3.4	3
4.	Fe/SNC	0.33	$0.5 \text{ M H}_2\text{SO}_4$	-	0.77 V	3.9	4
5.	ISAS-	0.50	$0.5 \text{ M H}_2\text{SO}_4$	-	0.773	3.87	5
	Co/HNCS						
6.	Fe-N/C	-	$0.5 \text{ M H}_2\text{SO}_4$	0.861 V	0.735	3.98	6
7.	Ru-N/G-750	0.326	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	0.89 V	0.75 V	3.9	7
8.	Cu-N-C	0.6	0.1 M KOH	-	0.869 V	3.97	8
9.	SA-Fe/NG	-	0.1 M KOH	-	0.8 V	3.83	9
10.	ZIF-8-900	0.63	0.1 M KOH	0.89 V	0.82 V	-	10
11.	25% Cu-N/C		0.1 M KOH	0.915 V	0.813 V	3.94	11
12.	Co/graphene	0.6	$0.5 \text{ M H}_2\text{SO}_4$	0.80 V	0.75 V	-	12
	sheets						
13.	ZIF-derived	-	0.1 M KOH	0.83 V	-	3.3	13
	porous carbon						
	polyhedra						
14.	Ordered	0.5	0.1 M KOH	0.81 V	0.69 V	3.1	14
	mesoporous						
	carbon						

Table S2. ORR activity of MOF and MOF-derived Single-atom electrocatalysts from recently reported literature

Table S3. OER activity of MOF and MOF derived single atom electrocatalyst from recently reported literature

Sl. No.	Catalyst	Electrolyte	Onset Potential	η_{10}	Tafel	Ref
			(vs. RHE)			
1.	MOF3	0.5 M KOH	0.3625V	0.472 V	101	This work
2.	MOF3_A	0.5 M KOH	0.2955 V	0.424 V	99	This work
3.	$[Co(C_{12}H_6O_4)(H_2O)_4]$	0.1 M KOH	0.32 V	0.520 V	142	15
4.	Co-WOC-1	0.1 M KOH	0.390 V	-	128	16
5.	Cu-MOF	$0.5 \text{ M H}_2\text{SO}_4$	0.310 V	-	89	17
6.	Со-ТрВру	pH = 7	0.4 V	>0.5 V	59	18
7.	CoOx-ZIF	1.0 M KOH	-	0.318 V	70.3	19
8.	Co-ZIF-9	pH = 13.4	0.33 V	0.510 V	193	20
9.	NU-1000	pH = 11	0.476 V	0.566 V	-	21
10.	СоТРуР	0.1 M NaOH	-	0.40 V	-	22
11.	Co ₃ O ₄ C-NA	0.1 M KOH	0.290 V	_	70	15
12.	Ni-CN-200	1 M KOH	0.31 V	_	60	23
13.	Co-C ₃ N ₄ /CNT	1 M KOH	0.27 V	0.38 V	52.8	24

Schemes and Figures



Scheme S1. Synthetic route of Ligand H₂L.







Figure S1. ¹H (400 MHz, DMSO-d₆) spectrum of ligand H₂L.



Figure S2. ESI-MS spectra of ligand H₂L.



Figure S3. Asymmetric unit of MOF1.



Figure S4. (a) The coordination environment of $(Co)_2$ dimer formed within the assembly of MOF1; (b) representative coordination modes exhibited by H₂L in MOF1; (c) representation of coordination spheres around the Co(II) metal centers (Co1, Co2, Co3, and Co4 has the same environment, represented as Co).



Figure S5. The asymmetric unit of MOF2.



Figure S6. (a) A representation of coordination spheres around the Co(II) metal centers of MOF2; (b) representative coordination modes exhibited by H₂L and aip in MOF2; (c) CH... π interaction with the distance of 3.4568 Å forming sheet-like structure within the assembly of MOF2.



Figure S7. Asymmetric unit of MOF3.



Figure S8. (a) The coordination environment of Co_2 dimer formed within the assembly of MOF3; (b) representation of coordination environment around Co (II) metal center; (c) representative coordination modes exhibited by H₂L and aip in MOF3; (d) 3d polyhedral representation of MOF3.



Figure S9. Comparison of powder XRD pattern directly obtained from powder sample (experimental) with simulated pattern derives from single-crystal XRD in case of (a) MOF1, (b) MOF2, (c) MOF3.



Figure S10. IR spectra of (a) MOF1, (b) MOF2, and (c) MOF3.



Figure S11. Thermogravimetric analysis of (a) MOF1, (b) MOF2, (c) MOF3.



Figure S12. XPS spectra of different element (a) Co 2p, (b) N 1s, (O 1s) present in **MOF2_A** single-atom catalyst.



Figure S13. (a)-(e) TEM images of **MOF2** show the 2D nature of the ultrathin micron-sized layered material. (f) SAED pattern of the **MOF2** catalyst.



Figure S14. (a) AFM image of MOF catalyst (MOF2) and (b) its corresponding cross-sectional thickness profile.



Figure S15. EDS spectra (elemental composition is shown in the table) of (a) MOF2 & (b) MOF2_A.



Figure S16. SEM-EDS mapping image of MOF2_A.



Figure S17. I_D , I_G bands in Raman spectra of cobalt MOF catalyst (MOF2) and Co-single atom catalyst (MOF2_A).



Figure S18. N_2 adsorption/desorption isotherm of (a) cobalt MOF catalyst (**MOF2**) and (b) Co-single atom catalyst. The pore size distribution of (c) cobalt MOF catalyst (**MOF2**) and (d) Co-single atom catalyst. The Brunauer-Emmett-Teller (BET) equation was used to calculate the specific surface area. Pore size distributions were obtained using the Barrett Joyner-Halenda (BJH) method from the adsorption branch of the isotherm.



Figure S19. (a) Plots of ΔJ vs. scan rate for MOF2 and MOF2_A where the slope of the fitted line gives the corresponding C_{dl} values. Cyclic voltammograms of (a) MOF2 and (c) MOF2_A, sweeping over the potential from 1.05 V to 1.25 V (vs. RHE) for the determination of double-layer capacitance (C_{dl}) and thereby estimation of effective surface area (ECSA).



Figure S20. ORR polarization curve at different rotating speeds for (a) MOF1, (c) MOF2 (e) MOF3; ORR stability plot of taking linear sweep voltammogram after the different number of potential cycles have been plotted for (b) MOF1, (d) MOF2 (f) MOF3. ORR voltammograms of MOF catalysts were recorded at a rotation rate of 1600 rpm in O_2 saturated 0.1 M KOH using RDE.



Figure S21. ORR polarization curve at different rotating speeds for (a) **MOF2_A**, (c) **MOF3_A**; ORR stability plot of taking linear sweep voltammogram after the different number of potential cycles have been plotted for (a) **MOF2_A**, (c) **MOF3_A**. ORR voltammograms of MOF-derived single-atom catalysts were recorded at a rotation rate of 1600 rpm in O₂ saturated 0.1 M KOH using RDE.



Figure S22. Post electrochemical low-resolution TEM images of (a-c) cobalt MOF catalyst (**MOF2**) and (e-g) Co-single atom catalyst (**MOF2_A**).



Figure 23. Post electrochemical powder XRD of cobalt MOF catalyst (MOF2) and (e-g) Cosingle atom catalyst (MOF2_A).



Figure S24. Tafel plots derived from LSVs taken for OER in 0.5 M KOH of all Co-MOF-based catalysts.



Figure S25. OER accelerated degradation stability testing for (a) MOF2, (b) MOF3, (c) MOF2_A, and (d) MOF3_A.

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