Electronic Supplementary Material (ESI) for Materials Advances.

Electrocataytic water oxidation from a mixed linker MOF based on NU-1000 with an integrated ruthenium-based metallo-linker

Andrew Howe[a,b], Timofey Liseev[a], Marcos Gil-Sepulcre[b], Carolina Gimbert-Suriñach[b], Jordi Benet-Buchholz[b], Antoni Llobet[b] and Sascha Ott*[,a]

[a.] *Department of Chemistry – Ångström Laboratory; Uppsala University; Box 523; 75120 Uppsala; Sweden.*
[b.] *Institute of Chemical Research of Catalonia (ICIQ), Barcelona Institute of Science and Technology (BIST), Av. Països Catalans 16, 43007, Tarragona, Spain.*

Supplementary Information

Contents

General Methods, Materials and Instrumentation.

All chemicals were purchased from commercial suppliers (Sigma-Aldrich, VWR, Fluorochem, and Alfa-Aesar) and used without further purification, unless stated otherwise. Solvents were dried using appropriate drying agents (sodium for diethyl ether and THF; calcium hydride for dichloromethane and acetonitrile) and freshly distilled under argon before use. 2,2′:6′,2″-*terpyridine-6,6”-dicarboxylic acid*, (4,4'-(pyridine-3,5-diyl)dibenzoic acid), 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrabenzoic acid) and Ru(tda)(dmso)OH_2 were synthesised according to existing literature methods.[1-4]

^{1}H and ^{13}C NMR spectra were measured using a JEOL 400 MHz spectrometer at 298 K. Powder X-ray diffraction patterns (PXRD) were obtained using a Simons D5000 Diffractometer (Cu Kα, λ = 0.15418 nm) at 45 kV and 40 mA, using a step size of 0.02°.

The scanning electron microscopy (SEM) images were taken by a Leo 1550 FEG microscope (Zeiss, Oberjochen, Germany) equipped with an in-lens detector at between 2.5 - 15 kV acceleration voltage. Energy-dispersive X-ray (EDX) data was collected with an 80 mm^2 Silicon Drift Detector using AZtec (INCA energy) software at a working distance of 8.5 nm.

Brunauer–Emmett–Teller (BET) isotherm were used for surface area measurements were carried out using a Micromeritics ASAP 2060 and the N_2 absorption isotherm was recorded at 77 K. Prior to measurement, materials were activated under dynamic vacuum at 80°C (1×10^{-4} Pa) using a Micromeritic SmartVacPrep sample preparation unit. The BET surface area reported was calculated by the proprietary ASAP software.

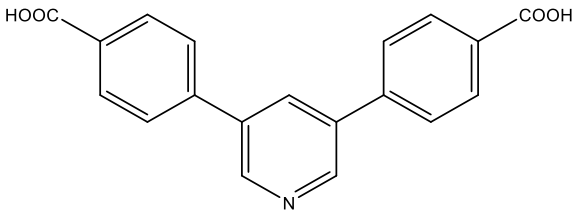
Metal content of the MOF was quantified by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Spectro Ciros ICP-OES system (Kleve, Germany) equipped with charge coupled device (CCD) detector, clyonic spray chamber, and modified-Lichte nebulizer. The operating conditions: 14.0 L/min coolant Ar gas, 0.9 L/min plasma Ar gas and 0.9 L/min nebulizer Ar gas. MOF Digestion prior to ICP analysis: 1 mg of MOF were added to 0.5 mL 30 % H_2O_2 with 4.5 mL of HNO_3 3%) mixture, sealed with a stirrer bar and microwaved for 15 minutes at 100°C. This was filtered and volume made up to 5mL in a volumetric flask.

Cyclic voltammetry (CV) measurements were performed using a single compartment cell. For solution phase measurements, a conventional three electrode set up using a GC disk working (0.071 cm^2) electrode, a glassy carbon counter electrode, and Ag/AgCl reference electrode (+0.2 V referenced to NHE), connected to Metrohm Autolab potentiostat (PGSTAT302) with a GPES electrochemical interface. 0.1 M phosphate buffer solution (phbs) was used as the supporting electrolyte.

Measurements at different pH values were carried out in solution-phase measurements of the linker were performed at a concentration of 1 mM in 0.1 M phosphate buffer solution (pH 1 to 10), using Ag/AgCl(3 M KCl) and $HgSO_4$ electrode (+0.2 V and +0.65 vs NHE respectively) was used as reference electrode which was referenced regularly using ferrocene carboxylic acid (0.28 V vs. Ag/AgCl 3M KCl) and Controlled Potential Electrolysis (CPE) for oxygen evolution reaction (OER) were performed using a two-compartment H-cell (Pine Research) connected by a glass frit. A platinum coil was used as counter electrode. Typically, the volume of electrolyte in the working and counter compartment was 15 mL.

S1. Synthesis and Characterization

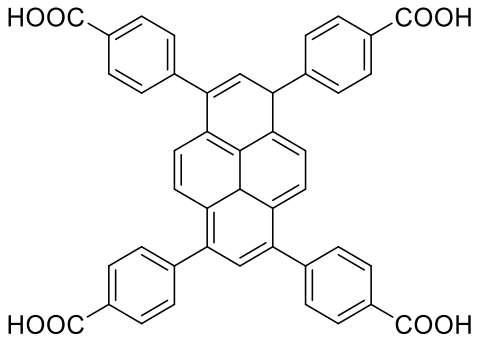
Synthesis of 4,4'-(pyridine-3,5-diyl)dibenzoic acid



This procedure was found in the literature[2]. In a 100 mL twin-necked round bottomed flask, 1 g of 3,5-dibromo pyridine, 1.8 g of 4-methoxycarbonyl boronic acid, 2.4 g sodium carbonate and 111 mg of tetrakis(triphenylphosphine) palladium(0) was weighed out and a stirrer bar added. The flask was sealed with a septum and a reflux condenser and purged with argon. 70 mL degassed dioxane/water (64 mL:6 mL) (11:1) was introduced via cannulation and refluxed for 3 days. The solvent was removed under reduced pressure and the flask was washed out with chloroform and washed through a pad of celite. The diester was subsequently purified via column chromatography using a mixture of hexane/EtOAc (4:1 – 1:1). The diester was subsequently suspended in 20 mL of 10% NaOH in water solution and refluxed overnight. This solvent was removed under reduced pressure and the residue dissolved in 5 mL of hot water and acidified to pH of 3 using HCl. The formed precipitate was collected and subsequently washed with water and acetonitrile to yield 958 mg of product (71 % yield)

^{1}H NMR (500 MHz, DMSO-d_6) δ 9.15 (d, J = 2.0 Hz, 2H), 8.79 (t, J = 2.0 Hz, 1H), 8.09 (d, J = 0.8 Hz, 8H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 167.84, 145.02, 140.53, 137.01, 131.97, 130.93, 128.64. Calc. for [M], ($C_{19}H_{13}NO_2$):319.32, Found: 319.0.

Synthesis of 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrabenzoic acid

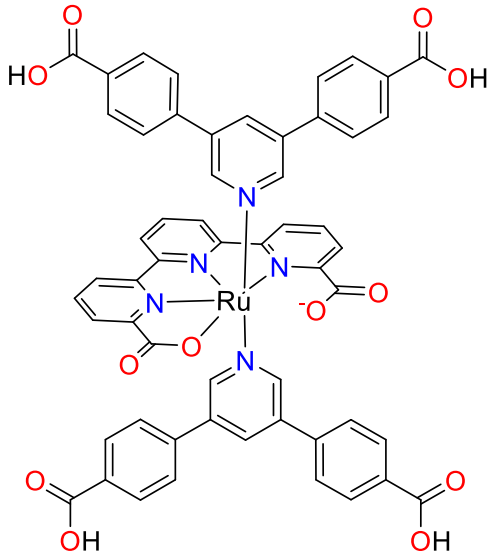


Synthesized according to adapted literature procedure[3]. In a 100 mL twin-necked round bottomed flask, (4-(methoxycarbonyl)phenyl)boronic acid (1 eq, 6 mmol), 1,3,6,8 tetrabromopyrene (1 eq, 0.97 mmol), tetrakis(triphenylphosphine) palladium(0) (0.03 eq, 0.026 mmol), and potassium phosphate tribasic (5.4 eq, 5.40 mmol) was weighed out and a stirrer bar added. The flask was sealed with a septum and a reflux condenser and purged with argon. Dry and degassed dioxane (30 mL) was introduced using a syringe and the reaction was refluxed for 72 h in an oil bath. The

reaction mixture was washed with water and extracted with chloroform three times (3 x 50 mL). The chloroform was removed under vacuum, and 50 ml of dioxane/H_2O (20:30) was added along with 2 g (50 mmol) of sodium hydroxide. This suspension was refluxed and stirred vigorously overnight. The solvents were removed under vacuum, 20 mL of deionized water was added and the pH adjusted to pH 3 using HCl. The resulting yellow solid was washed with water (15 mL x 3) and chloroform (10 mL x 3). The yellow solid was dissolved with the minimum amount of hot DMF. Around ten times the volume of MeOH was added to DMF solution, allowed to cool and filtered. The filtrate was washed with methanol and dried. This gave 0.53g (79%) of pure H_4TBAPy as the product

^{1}H NMR (DMSO-d6): δ 7.86 (d, 8H), 8.09 (s, 2H), 8.17 (d, 8H), 8.21 (s, 4H), 13.12 (s, 4H).

Synthesis of Rutda(4,4'-(pyridine-3,5-diyl)dibenzoic acid)$_2$, **1**



The tda ligand was synthesized according to a previous method[1], with the Ru(tda)(dmso)OH_2 made according to literature methods[4]. In a 25 mL twin-necked round bottomed flask, 30 mg (1 eq, 0.06 mmol) of RuTda(dmso)OH_2 and 58 mg (2 eq, 0.12 mmol) and 16 mg (4.4 mmol,0.445 mmol) of sodium hydroxide was weighed out and a stirrer bar added. The flask was sealed with a septum and a reflux condenser and purged with argon. 5 mL of degassed water was added and stirred at reflux for one day. This was acidified to pH 3 using 2M HCl and left in the fridge for one hour to precipitate. Thie precipitate was collected by centrifugation and washed with water (45 ml × 3), methanol (45 mL × 3) and ethanol (45 mL × 3). This was subsequently dissolved in hot ethanol and precipitated with ether to yield **1** in 24.1 mg (34% yield).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.83 (d, J = 8.1 Hz, 2H), 8.61 (d, J = 8.0 Hz, 2H), 8.48 (s, 4H), 8.29 (s, 2H), 8.20 (t, J = 8.0 Hz, 1H), 8.00 (d, J = 8.1 Hz, 10H), 7.81 (dd, J = 18.3, 7.7 Hz, 10H). ^{13}C NMR (126 MHz, DMSO-d6) δ 169.89, 167.34, 161.76, 160.52, 157.55, 150.35, 139.59, 137.03, 135.87, 133.88, 133.04, 131.67, 130.39, 127.86, 126.04, 124.54, 123.92. Calc. for [M], ($C_{55}H_{35}N_5O_{12}Ru$): 1058.98, found 1060. Elemental Analysis (% Found): N (5.47 %), C (53.2 %), H (3 %). Calcd for $C_{55}H_{35}N_5O_{12}Ru$, C (62.38 %), H (3.33 %), N (6.61 %); O (18.13 %) and Ru (9.54 %).

Mixed-Linker MOF Synthesis

NU-1000 synthesis

The solvothermal mixed-linker synthesis procedure: in a 20 mL screw-cap vial, 98 mg (0.3 mmol, 1 eq) of $ZrOCl_2.8H_2O$ and 2 g (16.38 mmol, 54.6 eq) benzoic acid was weighed out and 8 mL of dry DMF was added via syringe and the vial was sealed and sonicated for three minutes. This vial was subsequently placed into the oven at 80°C for one hour. The vial is taken out of the oven and allowed to cool to room temperature. 40 mg (0.06 mmol, 0.2 eq) of H_4TBAPy and 40 µL (0.52 mmol, 1.73 eq) of trifluoroacetic acid was added, vial sealed and sonicated for 15 minutes. This was placed into a temperature-controlled oven at 100°C for 18 hours.

a *(5 mol % mixed linker synthesis)*

The solvothermal mixed-linker synthesis procedure: in a 20 mL screw-cap vial, 49 mg (0.152 mmol, 1 eq) of $ZrOCl_2.8H_2O$ and 1.34 g (10.946 mmol, 72 eq) benzoic acid was weighed out and 12 mL of dry DMF was added via syringe and the vial was sealed and sonicated for three minutes. This vial was subsequently placed into the oven at 80°C for one hour. The vial is taken out of the oven and allowed to cool to room temperature. 20 mg (0.0526 mmol, 0.35 eq) of H_4TBAPy and 8.1 mg (0.0076 mmol, 0.05 eq) of Rutda(4,4'-(pyridine-3,5-diyl)dibenzoic acid)$_2$ was added, vial sealed and sonicated for 15 minutes. This was placed into a temperature-controlled oven at 100°C for three days.

b *(10 mol % mixed linker synthesis)*

The solvothermal mixed-linker synthesis procedure: in a 20 mL screw-cap vial, 49 mg (0.152 mmol, 1 eq) of $ZrOCl_2.8H_2O$ and 1.34 g (10.946 mmol, 72 eq) benzoic acid was weighed out and 12 mL of dry DMF was added via syringe and the vial was sealed and sonicated for three minutes. This vial was subsequently placed into the oven at 80°C for one hour. The vial is taken out of the oven and allowed to cool to room temperature. 20 mg (0.0526 mmol, 0.35 eq) of H_4TBAPy and 16.2 mg (0.0152 mmol, 0.1 eq) of Rutda(4,4'-(pyridine-3,5-diyl)dibenzoic acid)$_2$ was added, vial sealed and sonicated for 15 minutes. This was placed into a temperature-controlled oven at 100°C for three days.

c (*15 mol % mixed linker synthesis)*

The solvothermal mixed-linker synthesis procedure: in a 20 mL screw-cap vial, 49 mg (0.152 mmol, 1 eq) of $ZrOCl_2.8H_2O$ and 1.34 g (10.946 mmol, 72 eq) benzoic acid was weighed out and 12 mL of dry DMF was added via syringe and the vial was sealed and sonicated for three minutes. This vial was subsequently placed into the oven at 80°C for one hour. The vial is taken out of the oven and allowed to cool to room temperature. 20 mg (0.0526 mmol, 0.35 eq) of H_4TBAPy and 24 mg (0.0228 mmol, 0.15 eq) of Rutda(4,4'-(pyridine-3,5-diyl)dibenzoic acid)$_2$ was added, vial sealed and sonicated for 15 minutes. This was placed into a temperature-controlled oven at 100°C for three days.

d *(20 mol % mixed linker synthesis)*

The solvothermal mixed-linker synthesis procedure: in a 20 mL screw-cap vial, 49 mg (0.152 mmol, 1 eq) of $ZrOCl_2.8H_2O$ and 1.34 g (10.946 mmol, 72 eq) benzoic acid was weighed out and 12 mL of dry DMF was added via syringe and the vial was sealed and sonicated for three minutes. This vial was subsequently placed into the oven at 80°C for one hour. The vial is taken out of the

oven and allowed to cool to room temperature. 20 mg (0.0526 mmol, 0.35 eq) of H4TBAPy and 32 mg (0.0304 mmol, 0.20 eq) of Rutda(4,4'-(pyridine-3,5-diyl)dibenzoic acid)$_2$ was added, vial sealed and sonicated for 15 minutes. This was placed into a temperature-controlled oven at 100°C for three days.

e *(25 mol % mixed linker synthesis)*

The solvothermal mixed-linker synthesis procedure: in a 20 mL screw-cap vial, 49 mg (0.152 mmol, 1 eq) of $ZrOCl_2.8H_2O$ and 1.34 g (10.946 mmol, 72 eq) benzoic acid was weighed out and 12 mL of dry DMF was added via syringe and the vial was sealed and sonicated for three minutes. This vial was subsequently placed into the oven at 80°C for one hour. The vial is taken out of the oven and allowed to cool to room temperature. 20 mg (0.0526 mmol, 0.35 eq) of H_4TBAPy and 40 mg (0.038 mmol, 0.25 eq) of Rutda(4,4'-(pyridine-3,5-diyl)dibenzoic acid)$_2$ was added, vial sealed and sonicated for 15 minutes. This was placed into a temperature-controlled oven at 100°C for three days.

f *(30 mol % mixed linker synthesis)*

The solvothermal mixed-linker synthesis procedure: in a 20 mL screw-cap vial, 49 mg (0.152 mmol, 1 eq) of $ZrOCl_2.8H_2O$ and 1.34 g (10.946 mmol, 72 eq) benzoic acid was weighed out and 12 mL of dry DMF was added via syringe and the vial was sealed and sonicated for three minutes. This vial was subsequently placed into the oven at 80°C for one hour. The vial is taken out of the oven and allowed to cool to room temperature. 20 mg (0.0526 mmol, 0.35 eq) of H_4TBAPy and 48 mg (0.0456 mmol, 0.3 eq) of Rutda(4,4'-(pyridine-3,5-diyl)dibenzoic acid)$_2$ was added, vial sealed and sonicated for 15 minutes. This was placed into a temperature-controlled oven at 100°C for three days.

Standard washing procedure consisted of three washing cycles with DMF and two with DCM. A washing cycle consisted of centrifugation to separate the solid from the previous supernatant, followed by resuspension in the next washing solvent and leaving to exchange for one day. After the last washing cycle with DCM, the material was isolated and dried in vacuo overnight before further work

General Preparation of MOF@MWCNT Electrode

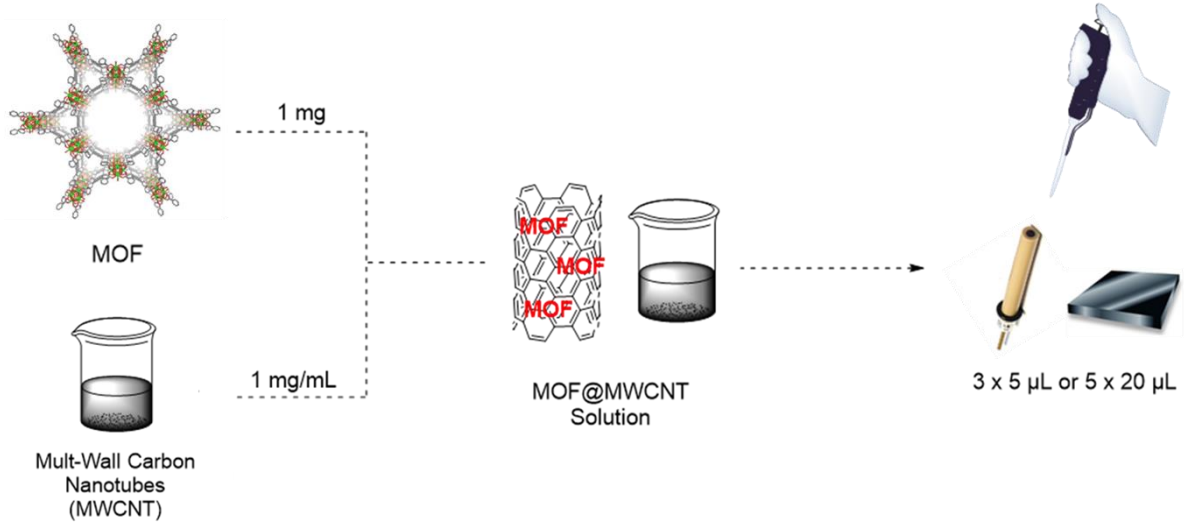


Figure S1. Preparation of MOF electrode via dropcasting

1 mg of MOF material is weighed out on an analytical balance. 1 mL of 1 mg/ml MWCNT solution (sonicated for 40 minutes) is added into the vial with 1 mg of MOF and sonicated together for 5 minutes. The GC plate is drop casted on both sides with the MOF@MWCNT (usually 3 x 5 µL for an electrode with a surface area of 0.07 cm^2 or 5 x 20 µL for a 0.5 cm^2 area) and allowed to dry under the fume hood for one hour. For electrochemical experiments samples were immobilized in MWCNTs on top of glassy carbon working electrodes and experiments were run in 0.1 M phosphate buffer electrolyte at pH = 7 at a v = 100 mV/s^{-1}.

S2. NMR spectroscopy

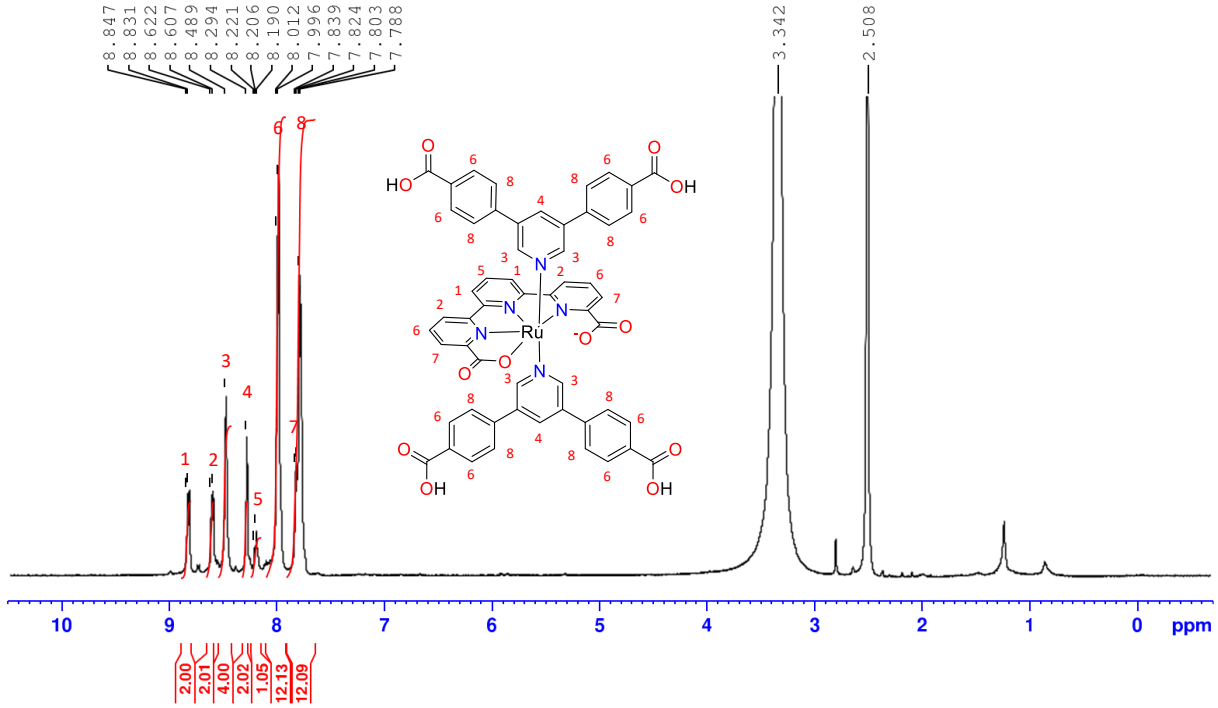


Figure S2. ^{1}H NMR of **1** in deuterated dimethyl sulfoxide (500 MHz, 298 K, [d_6]-DMSO).

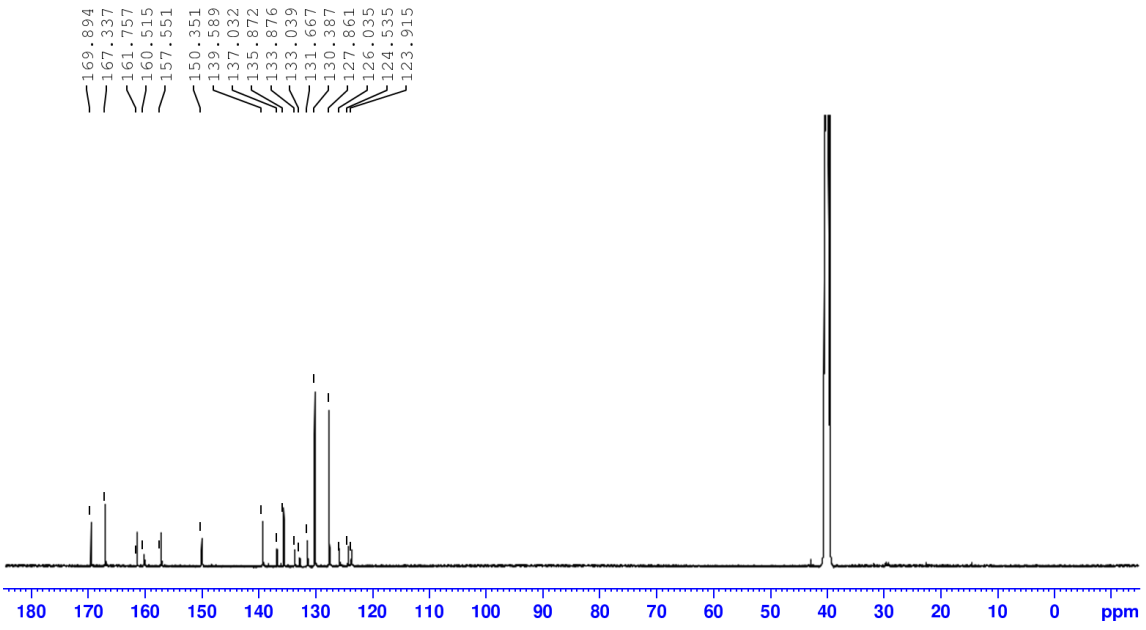


Figure S3. ^{13}C NMR of **1** in deuterated dimethyl sulfoxide (500 MHz, 298 K, [d_6]-DMSO).

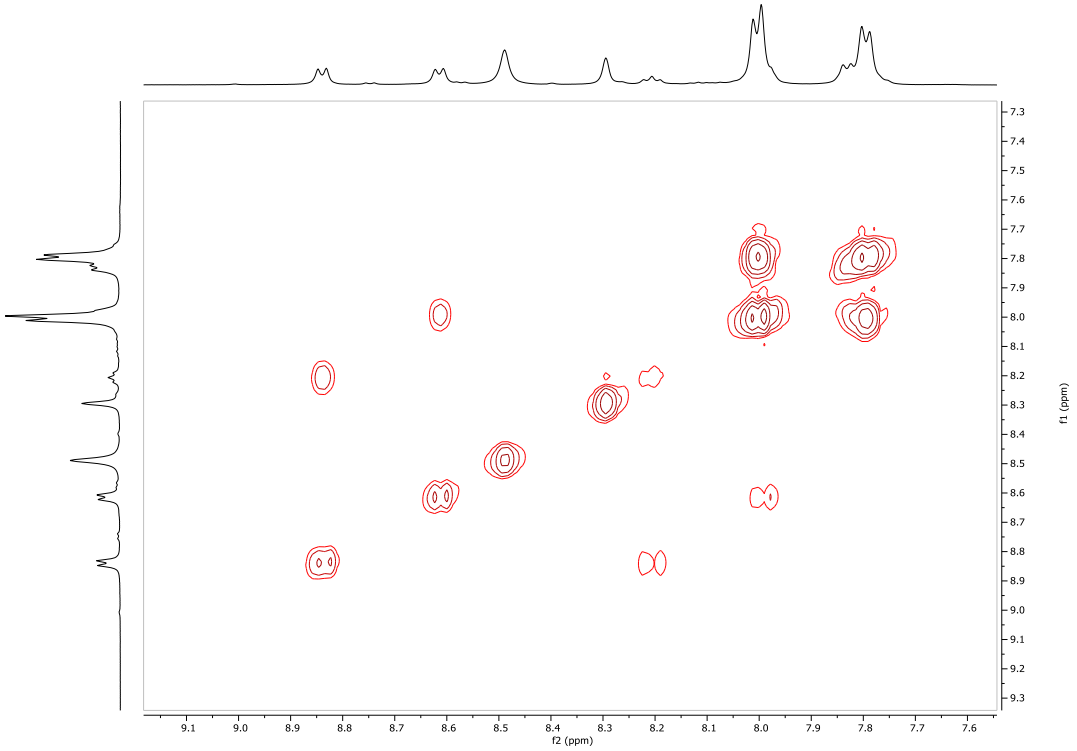


Figure S4. COSY 2D spectrum of **1** in deuterated dimethyl sulfoxide (500 MHz, 298 K, [d_6]-DMSO).

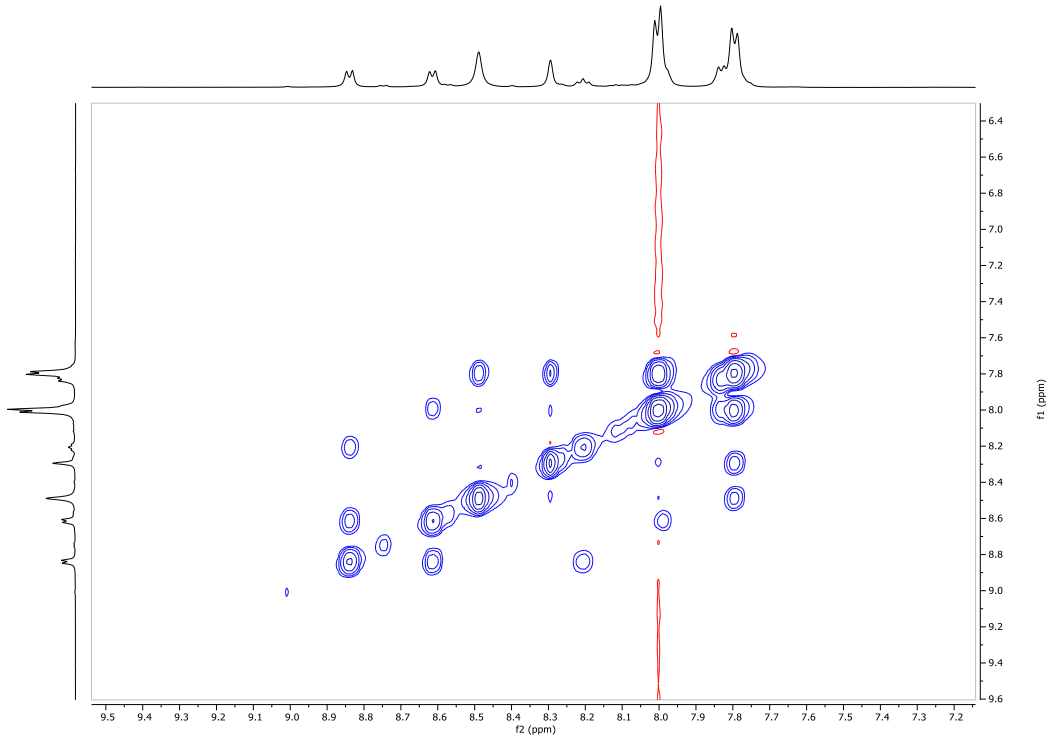


Figure S5. NOESY 2D spectrum of **1** in deuterated dimethyl sulfoxide (500 MHz, 298 K, [d_6]-DMSO).

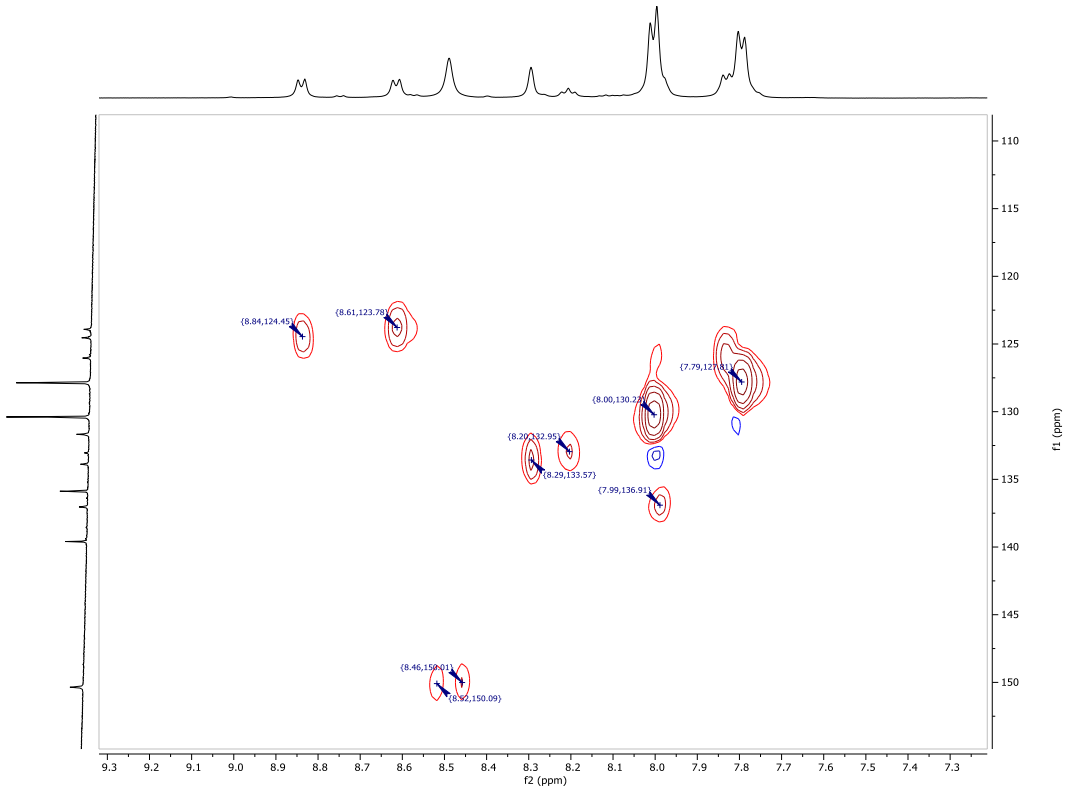


Figure S6. HSQC ^{1}H – ^{13}C 2D NMR spectrum of **1** in deuterated dimethyl sulfoxide (500 MHz, 298 K, [d_6]-DMSO).

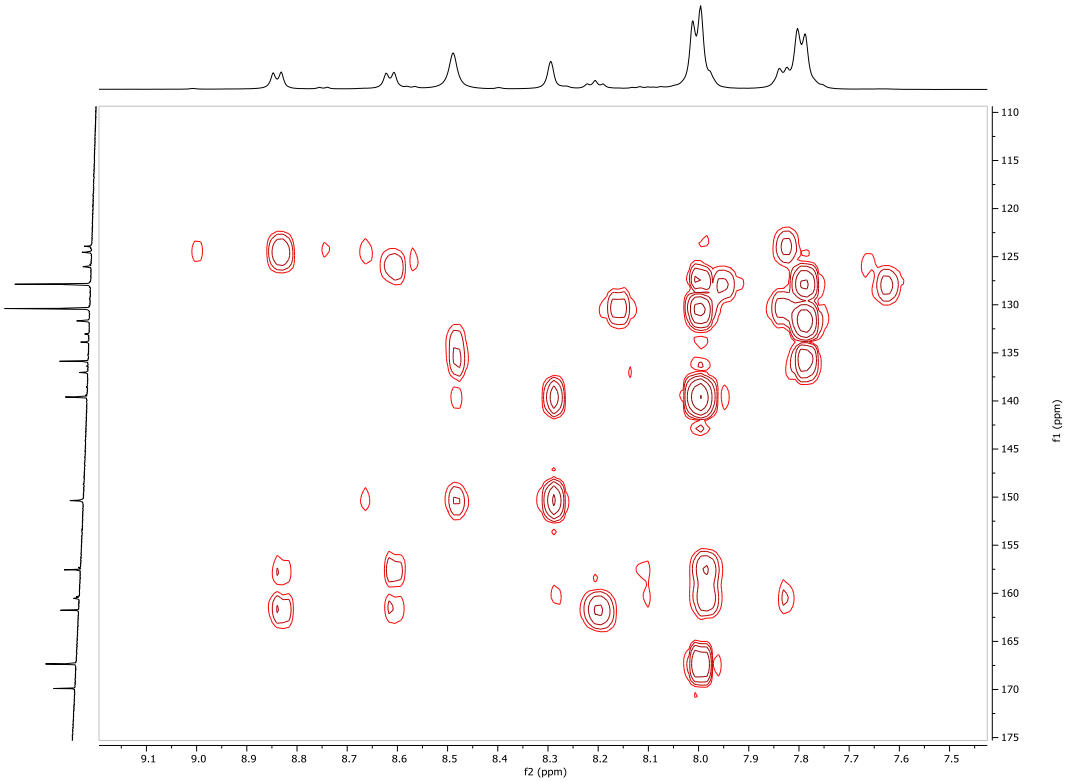


Figure S7. HMBC ^{1}H – ^{13}C 2D NMR spectrum of **1** in deuterated dimethyl sulfoxide (500 MHz, 298 K, [d_6]-DMSO).

S3. FT-IR spectroscopy

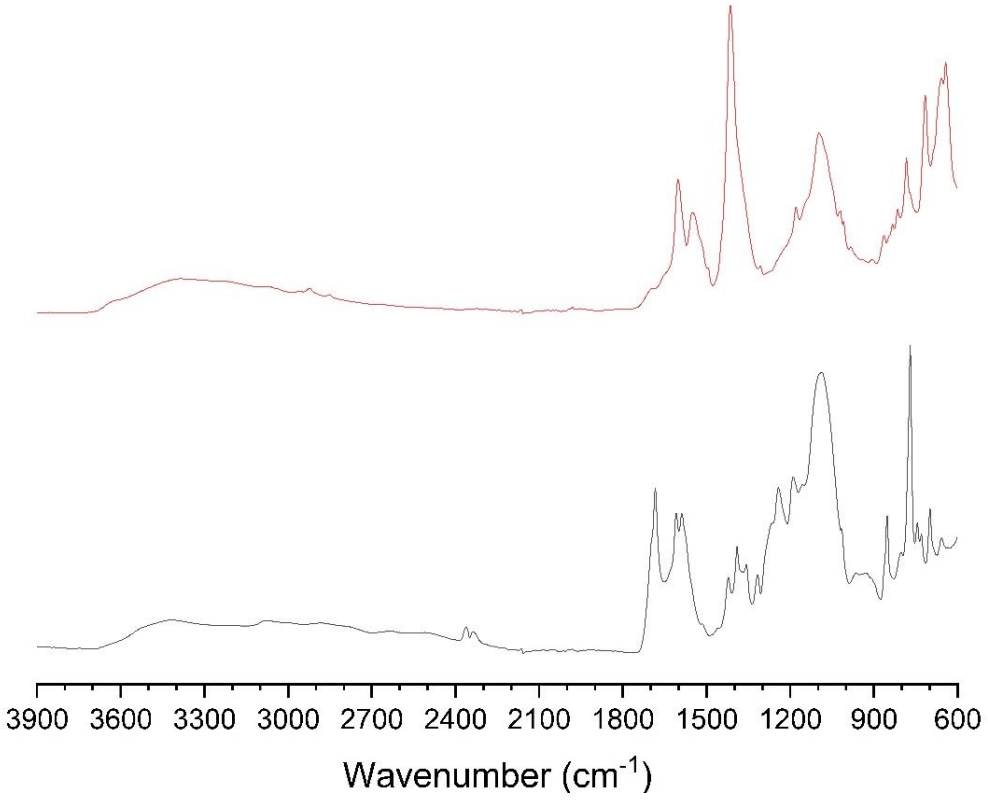


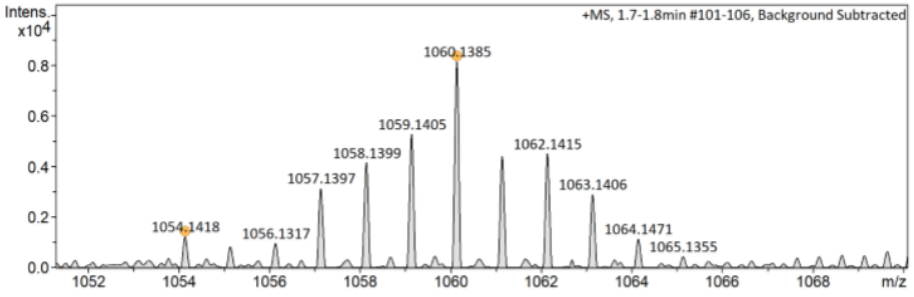
Figure S8. FT-IR of Mixed-Linker MOF and 1. 1 (red trace) vs **f** mixed-linker MOF (black trace).

S4. Elemental Analysis

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	5.4698	50	135157	RS	24.437340	.189841E+07
Carbon	53.1968	78	3302878	RS	1.000000	.476254E+07
Hydrogen	3.0083	239	535448	RS	6.168438	.129111E+08
Totals	61.6748		3973483			

Figure S9. Elemental analysis of **1.**

S5. Mass Spectroscopy



Meas. m/z	Ion Formula	m/z	|err| [ppm]	err [mDa]	mSigma	e¯ Conf	z
1054.1418	C55H36N5O12^96Ru	1054.1431	1.2	1.3	655.9	odd	1+
1060.1385	C55H36N5O12^102Ru	1060.1398	1.2	1.3	213.6	odd	1+

Figure S10. HRMS Mass spectrometry of 1.

S6. Single Crystal Diffraction

Crystal preparation: Crystals of **1** were grown in DMSO/DMF (by slow diffusion of Et_2O). The crystals were selected using a Zeiss stereomicroscope using polarized light and prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation.

Data collection: Crystal structure determination for sample **1** was carried out using a Apex DUO Kappa 4-axis goniometer equipped with an APPEX 2 4K CCD area detector, a Microfocus Source E025 IuS using MoK_α radiation, Quazar MX multilayer Optics as monochromator and an Oxford Cryosystems low temperature device Cryostream 700 plus (T = -173 °C). Full-sphere data collection was used with ω and φ scans. *Programs used:* Bruker Device: Data collection APEX-2 [5], data reduction Bruker Saint[6] V/.60A and absorption correction SADABS[7, 8].

Structure Solution and Refinement: Crystal structure solution was achieved using the computer program SHELXT[9]. Visualization was performed with the program SHELXle[10]. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F^2 using all measured intensities was carried out using the program SHELXL 2015[11]. All non-hydrogen atoms were refined including anisotropic displacement parameters.

Crystal Data Deposition: CCDC 2128791 contains the supplementary crystallographic data for this paper, **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures

Table S1. Crystal Data and Structure Refinement

Identification code	mo_ah153_0m_sq	
Empirical formula	C56 H38 N5 O12.50 Ru S0.50	
Formula weight	1098.01	
Temperature	100(2)K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 28.9776(11) Å	α = 90°.
	b = 17.2259(6) Å	β = 92.0682(14)°.
	c = 29.0901(12) Å	γ = 90°.
Volume	14511.3(10) $Å^3$	
Z	8	
Density (calculated)	1.005 Mg/m^3	
Absorption coefficient	0.280 mm^{-1}	
F(000)	4488	
Crystal size	0.300 x 0.200 x 0.010 mm^3	
Theta range for data collection	1.374 to 27.499°.	
Index ranges	-37<=h<=37,-19<=k<=22,-37<=l<=37	
Reflections collected	95661	
Independent reflections	33235[R(int) = 0.0605]	
Completeness to theta =27.499°	99.7%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.74 and 0.61	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	33235/ 819/ 1614	
Goodness-of-fit on F^2	1.010	
Final R indices [I>2sigma(I)]	R1 = 0.0568, wR2 = 0.1472	
R indices (all data)	R1 = 0.1153, wR2 = 0.1753	
Largest diff. peak and hole	1.828 and -0.649 $e.Å^{-3}$	

S7. ICP analysis of mixed-linker MOFs

Table S2. ICP analysis of mixed-linker MOFs. Determination of Zr and Ru content in mixed-linker MOF synthesis.

Sample	1	Zr Concentration (mg/L)	Ru Concentration (mg/L)	Ru Content
a	5 mol %	30.760	-	-
b	10 mol %	27.660	0.176	0.63%
c	15 mol %	31.240	0.495	1.56%
d	20 mol %	29.720	1.491	4.78%
e	25 mol %	27.910	1.210	4.16%
f	30 mol %	27.560	1.673	5.72%

S8. Scanning Electron Microscopy (SEM)

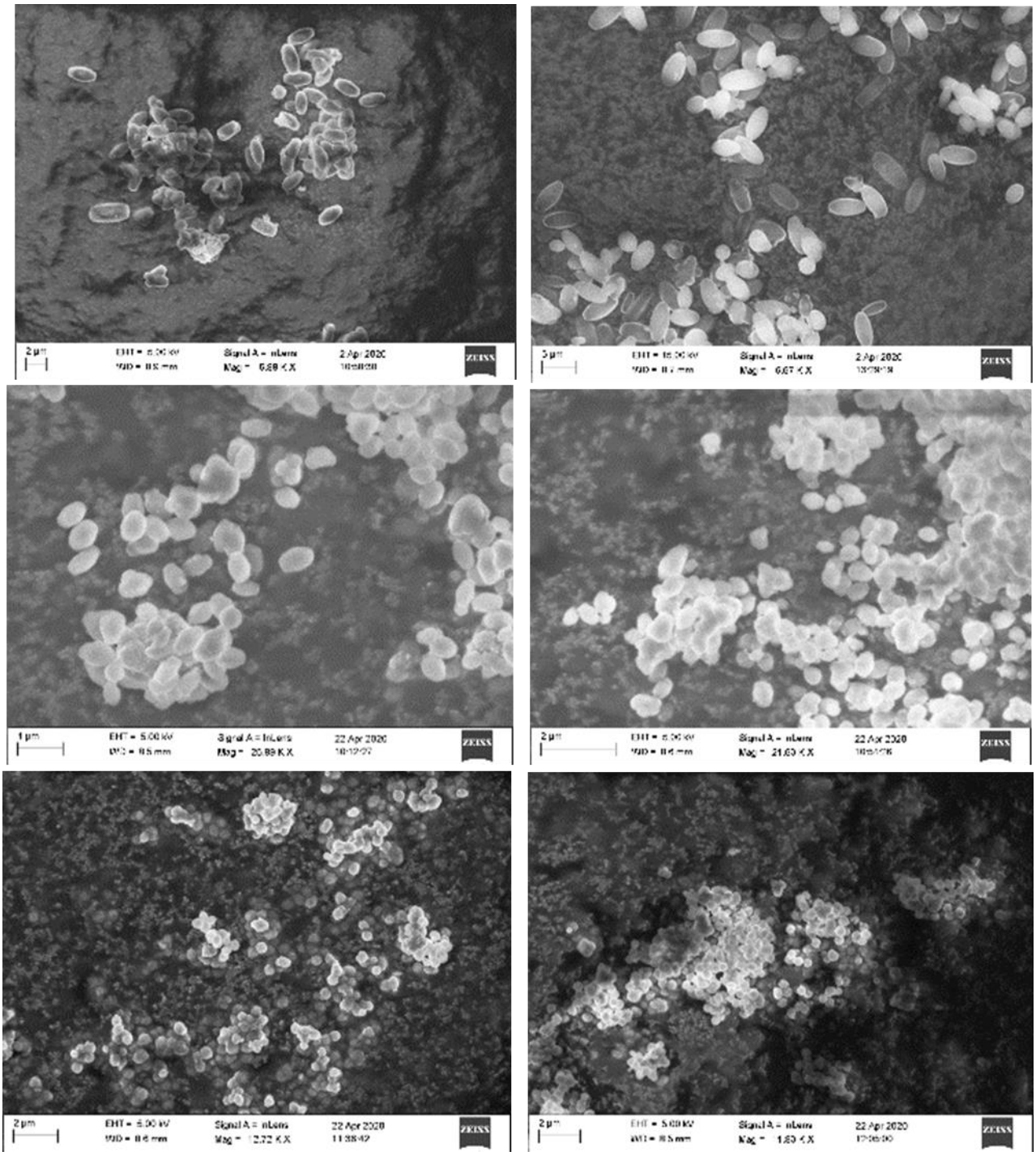


Figure S11. Scanning Electron Microscope (SEM) images of Rutda/H_4TBAPy mixed-linker MOFs. Top left – **a,** top right – **b,** middle left – **c,** middle right – **d,** bottom left – **e** and bottom right – **f**.

S9. Energy-Dispersive X-Ray (EDX)

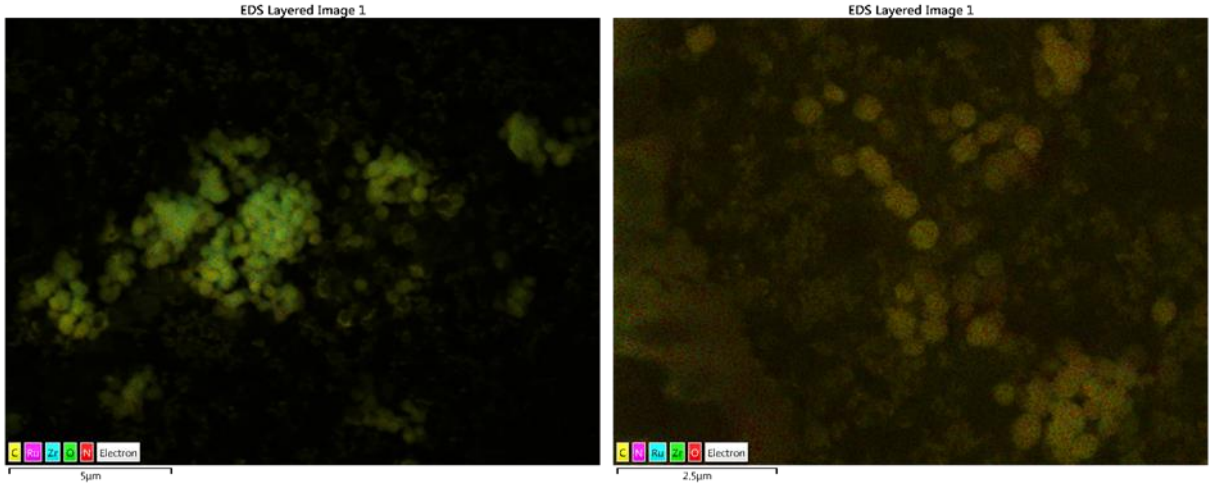


Figure S12. Energy-Dispersive X-Ray (EDX) images of **f**, with complex **1** incorporated into the mixed linker synthesis. The morphology and size of these MOF particles are influenced by the degree of ruthenium complex present during the synthesis.

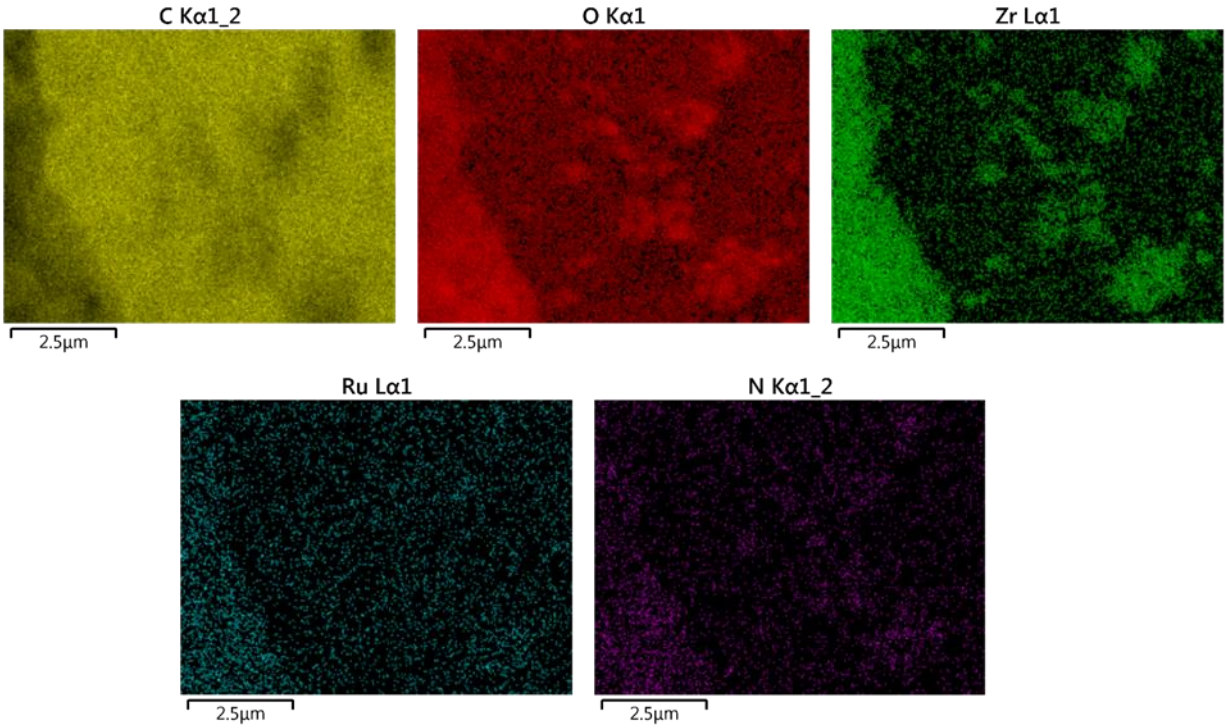


Figure S13. Energy-Dispersive X-Ray (EDX) images of **f**, with complex **1** incorporated into the mixed linker synthesis. These are the breakdown of the composition of the MOF by element, with the atoms of carbon, oxygen, zirconium, ruthenium and nitrogen visible in the EDX spectrum.

S10. BET Isotherms

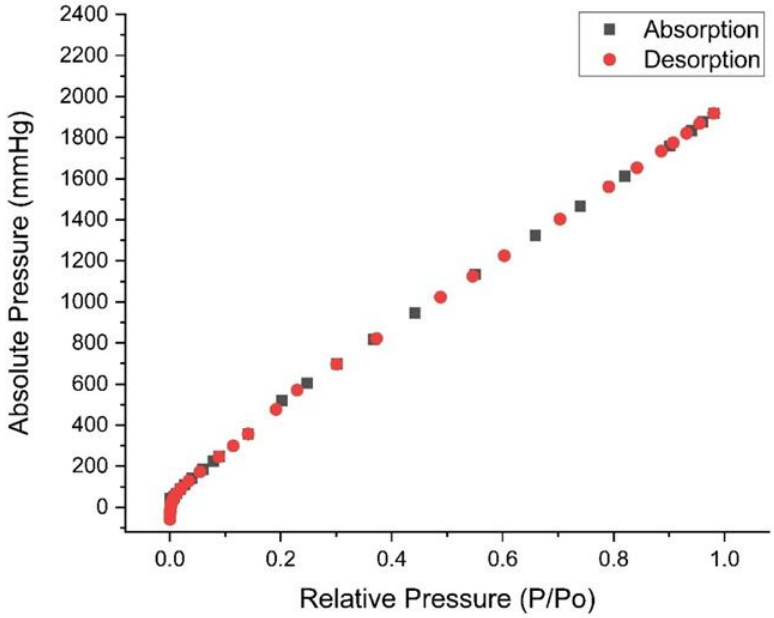


Figure S14. BET N_2 adsorption/desorption isotherm plot of **b**.

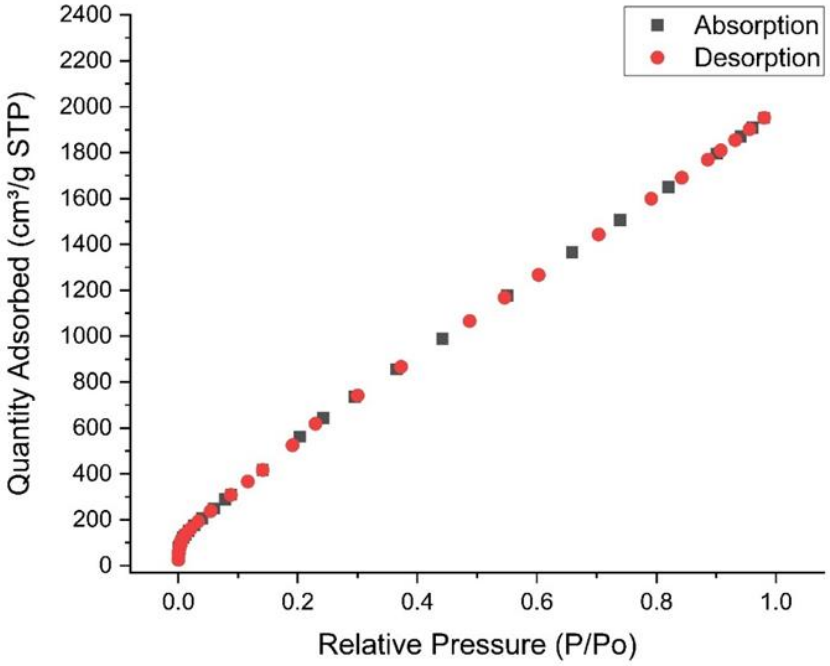


Figure S15. BET N_2 adsorption/desorption isotherm plot of **d**.

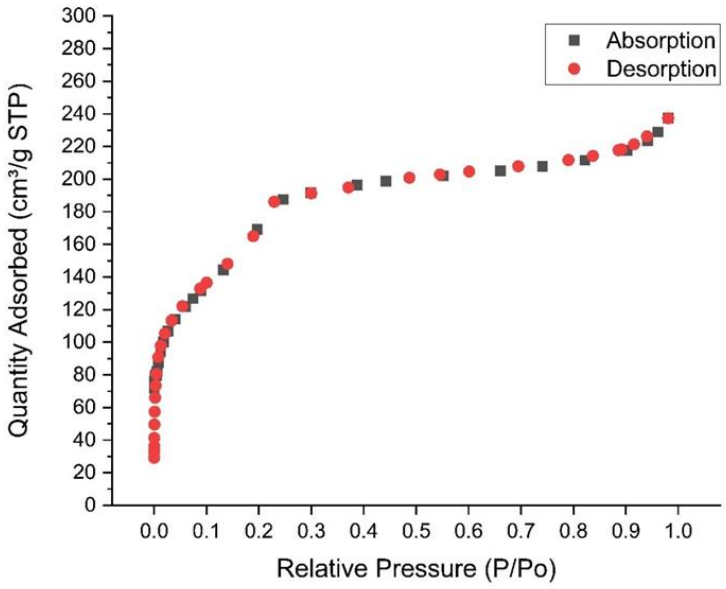


Figure S16. BET N_2 adsorption/desorption isotherm plot of **e**.

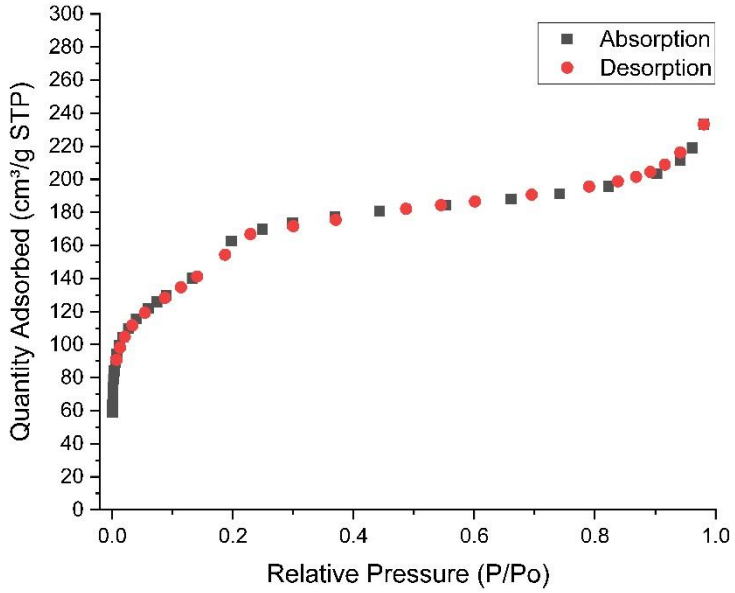


Figure S17. BET N_2 adsorption/desorption isotherm plot of **e**. *Note: Negative datapoints were omitted at (0,-55.49), (0, -62.29), (0, 63.9) and (0, -64.76). This anomaly is attributable to instrument error.

S11. Electrochemistry

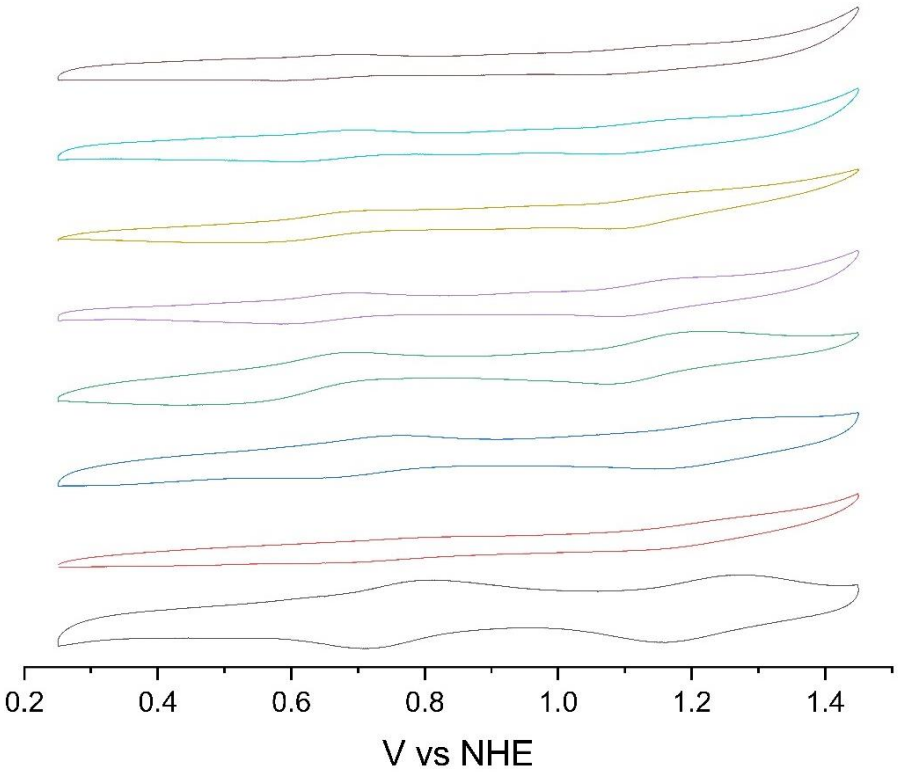


Figure S18. CV of **1** immobilized with MWCNT on a GC electrode, conducted at different pH values ranging from pH 1.66 to 10 in 0.1 M phosphate buffer solution (phbs). In each instance, two reversible redox couples can be observed. The redox events change, subject to pH conditions. 100 mV/s^{-1} CV pH 1.66 (black trace), 100 mV/s^{-1} CV pH 3.04 (red trace), 100 mV/s^{-1} CV pH 4.24 (light blue trace), 100 mV/s^{-1} CV pH 6 (green trace), 100 mV/s^{-1} CV pH 7.26 (purple trace), 100 mV/s^{-1} CV pH 8.07 (dark yellow), 100 mV/s^{-1} CV pH 9.06 (turquoise trace), 100 mV/s^{-1} CV pH 10.03 (coral trace).

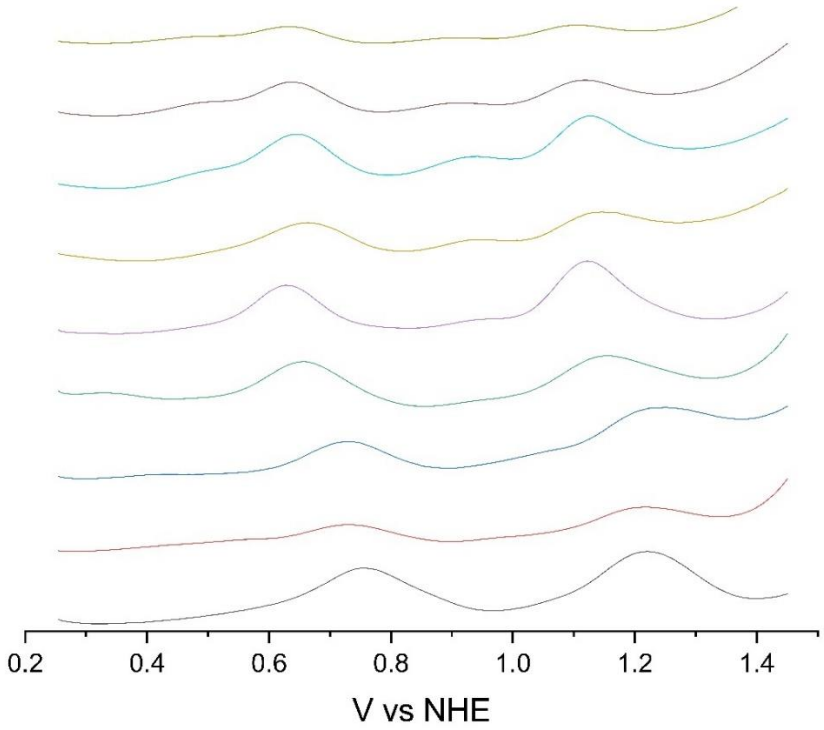


Figure S19. DPV of **1** immobilized on MWCNT, ranging from pH 1.66 to pH 10 in 0.1 M pH phosphate buffer solution, with 1 mM. DPV 0.1 M pH 1.66 (black trace), DPV 0.1 M pH 3.04 (red trace), DPV 0.1 M pH 4.04 (light blue trace), DPV 0.1 M pH 4.97 (green trace), DPV 0.1 M pH 6 (purple trace), DPV 0.1 M pH 7.07 (dark yellow), DPV 0.1 M pH 8.08 (turquoise trace), DPV 0.1 M pH 9.06 (coral trace), DPV 0.1 M pH 10.03 (tan trace).

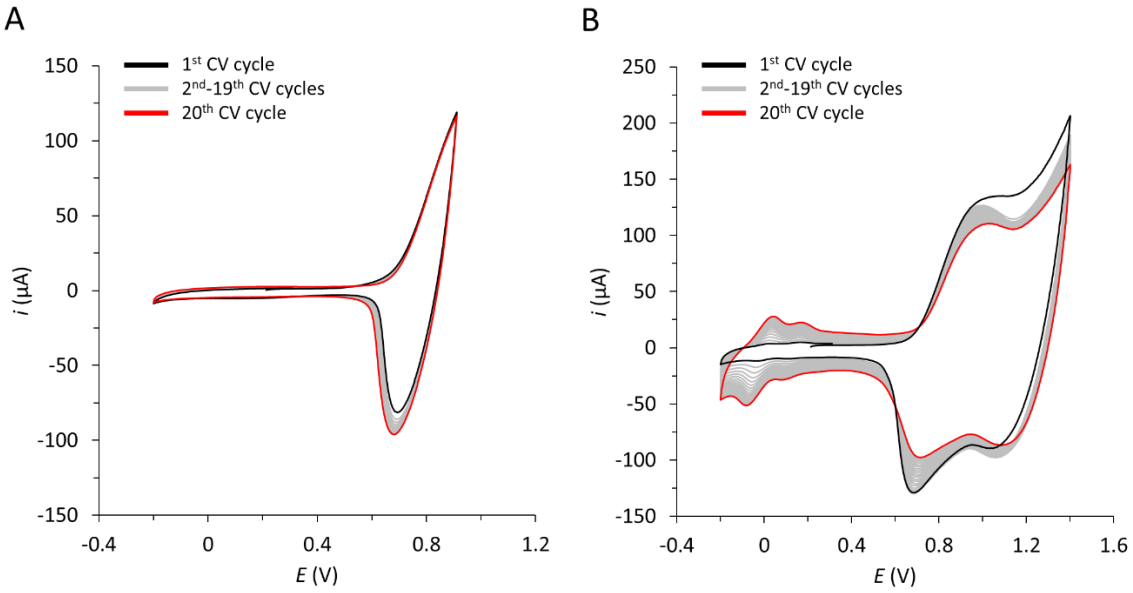


Figure S20. CV evolution of H_4TBAPy linker during 20 repetitive CV cycles with a scan range of -0.2 – 0.9 V (A) and -0.2 – 1.4 V (B). The black line corresponds to the first cycle, the grey line to the 2nd – 19th cycles and the red line to the 20th cycle. Conditions: 0.1 M phosphate buffer solution (pH 7), scan rate of 100 mV/s^{-1}.

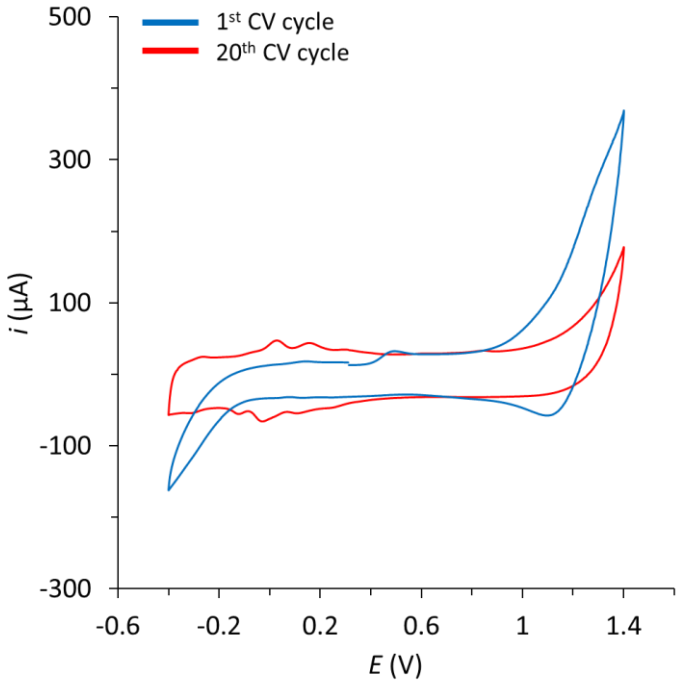


Figure S21. CV of NU-1000 before (blue line) and after (red line) 20 cycles. Conditions: 0.1 M phosphate buffer solution (pH 7), scan rate of 100 mV/s^{-1}.

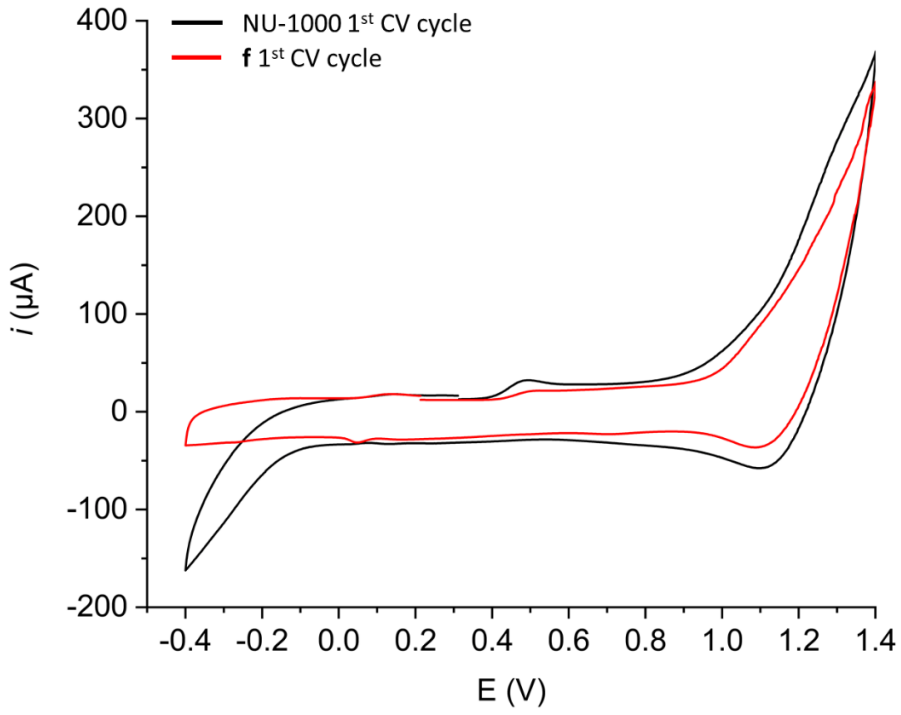


Figure S22. CV of 1st NU-1000 cycle (black line) and 1st cycle of mixed-linker **f** (red line). Conditions: 0.1 M phosphate buffer solution (pH 7), scan rate of 100 mV/s^{-1}.

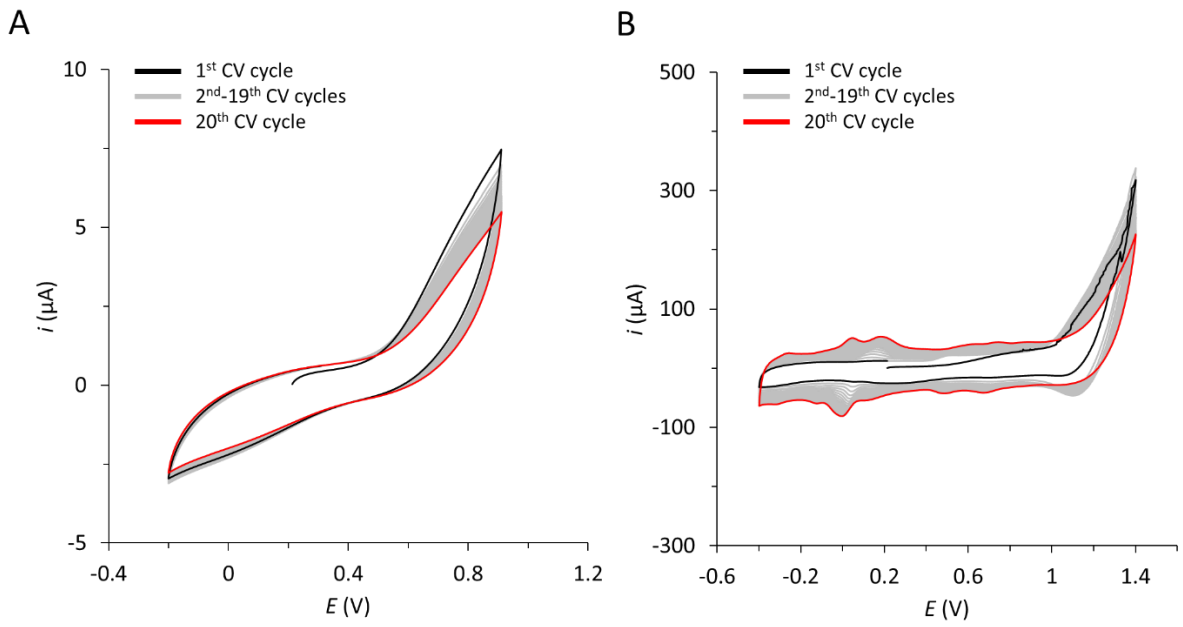


Figure S23. CV evolution of **f** during 20 repetitive CV cycles with a scan range of -0.2 – 0.9 V (A) and -0.2 – 1.4 V (B). The black line corresponds to the first cycle, the grey line to the 2nd – 19th cycles and the red line to the 20th cycle. Conditions: 0.1 M phosphate buffer solution (pH 7), scan rate of 100 mV/s^{-1}.

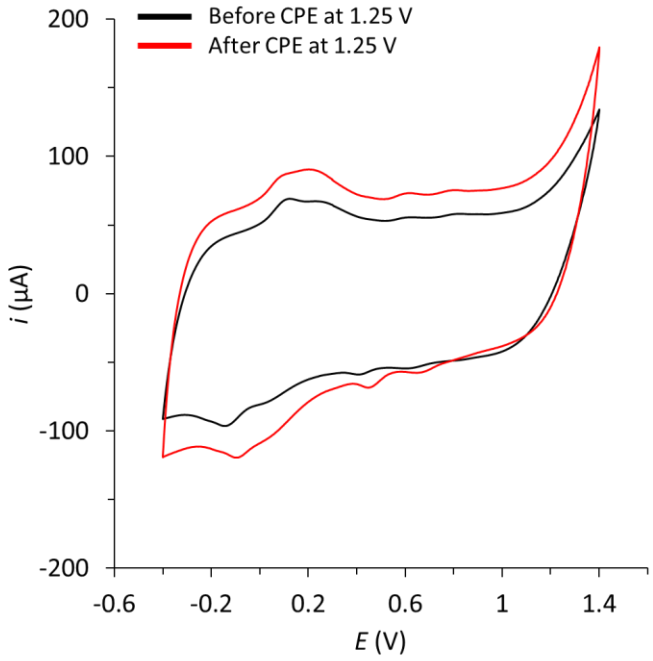


Figure S24. CV of **f** (after 50 scans in the range of -0.4 V to 1.4 V) before (black line) and after (red line) a CPE experiment at 1.25 V for 720 seconds. Conditions: 0.1 M phosphate buffer solution (pH 7), scan rate of 100 mV/s^{-1}.

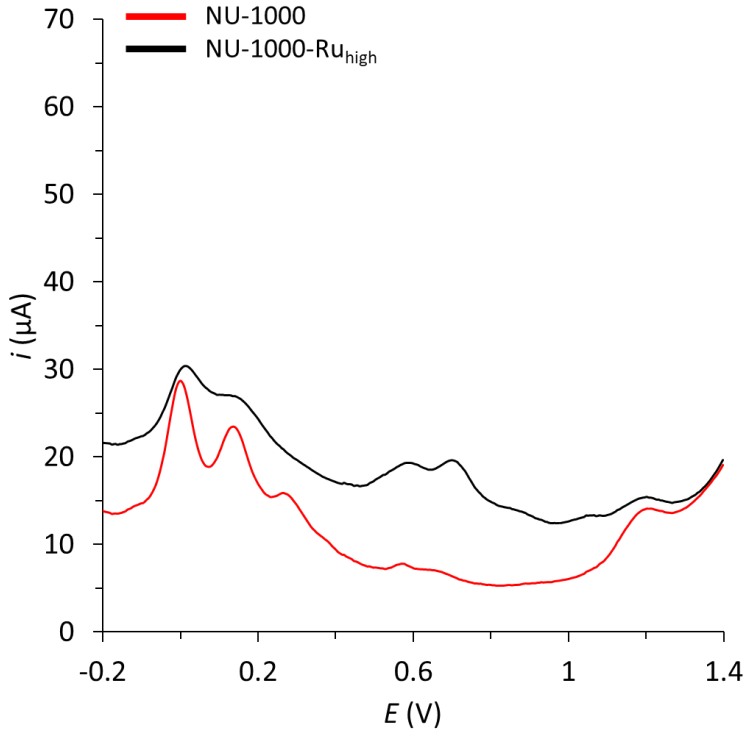


Figure S25. DPV of NU-1000 (red line) and **f** (black line). Conditions: 0.1 M phosphate buffer solution (pH 7), scan rate of 100 mV/s^{-1}.

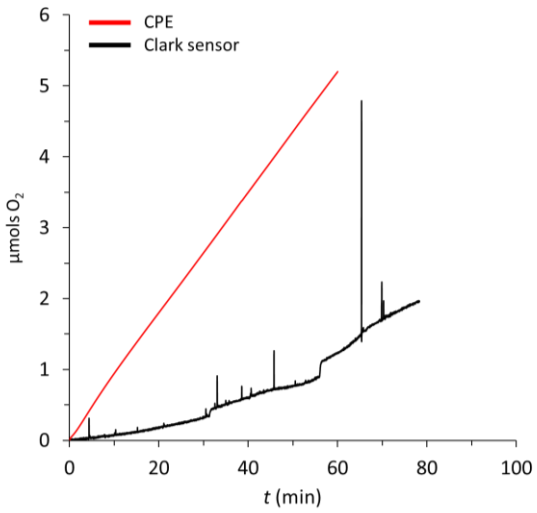


Figure S26. Oxygen evolution vs time for NU-1000-Ru_{high} during a CPE at 1.3 V *vs.* NHE in a 0.1 M phosphate buffer solution (pH 7), monitored with a gas phase Clark electrode. Black line corresponds to the O_2 measured with NU-1000-Ru_{high}; red line corresponds to the theoretical maximum based on the charge passed during the CPE (Q = 2.006 C). Faradaic efficiency was calculated from the amount of produced O_2, divided by the charge passed through the cell (Q = 2.006 C), giving rise to 37 % for NU-1000-Ru_{high}. The applied potential was stopped at 60-70 min, but the O_2 evolution continued until approx. 80 min due to trapped O_2 bubbles at the working electrode. Maximum TONs of 44600 for NU-1000-Ru_{high} were calculated from the Ru loading obtained by charge integration of the CV before CPE (Cat = 0.52 nmol/cm^2), and the surface area of the electrode (A = 0.078 cm^{-2}). This number should however only be seen as an upper limit, as most likely also Ru linkers in the crystal interior contribute to catalysis.

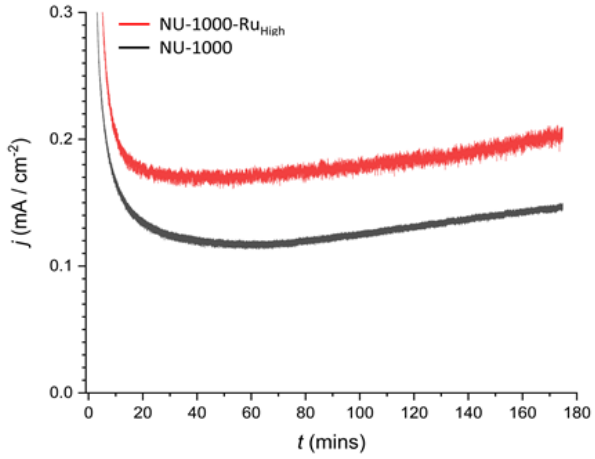


Figure S27. Long-term Controlled potential electrolysis of NU-1000-Ru_{high} (red line) and NU-1000 (black line) during a CPE at 1.3 V *vs.* NHE in a 0.1 M phosphate buffer solution (pH 7). The background oxidation of the NU-1000/nanotube electrode is non-productive in terms of water oxidation, and the current density about 2/3 of that of the NU-1000-Ru_{high} electrode. This ratio is similar to the reported Faradaic efficiency of 37%.

S12. References

1. Liseev, T.; Howe, A.; Hoque, M. A.; Gimbert-Suriñach, C.; Llobet, A.; Ott, S., Synthetic strategies to incorporate Ru-terpyridyl water oxidation catalysts into MOFs: direct synthesis vs. post-synthetic approach. *Dalton Transactions* **2020,** *49* (39), 13753-13759.
2. Yun, R.; Jiang, Y.; Luo, S.; Chen, C., Three-dimensional coordination polymers constructed from C2-symmetric linkers of pyridyl dicarboxylate ligands. *RSC Advances* **2014,** *4* (69), 36845-36848.
3. Mondloch, J. E.; Bury, W.; Fairen-Jimenez, D.; Kwon, S.; DeMarco, E. J.; Weston, M. H.; Sarjeant, A. A.; Nguyen, S. T.; Stair, P. C.; Snurr, R. Q.; Farha, O. K.; Hupp, J. T., Vapor-Phase Metalation by Atomic Layer Deposition in a Metal–Organic Framework. *Journal of the American Chemical Society* **2013,** *135* (28), 10294-10297.
4. Matheu, R.; Ertem, M. Z.; Benet-Buchholz, J.; Coronado, E.; Batista, V. S.; Sala, X.; Llobet, A., Intramolecular Proton Transfer Boosts Water Oxidation Catalyzed by a Ru Complex. *Journal of the American Chemical Society* **2015,** *137* (33), 10786-10795.
5. Bruker, *Data collection with APEX II version v2013.4-1*. Bruker AXS Inc: Madison, Wisconsin, USA, 2007.
6. Bruker, *Data reduction with Bruker SAINT version V8.30c*. Bruker AXS Inc: Madison, Wisconsin, USA, 2007.
7. Bruker, *SABABS: V2012/1*. Bruker AXS Inc: Madison, Wisconsin, USA, 2001.
8. Blessing, R. H., An empirical correction for absorption anisotropy. *Acta Cryst* **1995,** *A51*, 33 - 38.
9. Sheldrick, G. M., SHELXT – Integrated space-group and crystal-structure determination. *Acta Cryst* **2015,** *A71*, 3 - 8.
10. Huebschle, C. B., Sheldrick, G.M. & Dittrich, B. J, ShelXle: a Qt graphical ucer interface for SHELXL. *Appl. Cryst.* **2011,** *44*, 1281 - 1284.
11. Sheldrick, G. M., Crystal structure refinement with SHELXL. *Acta Cryst* **2015,** *C71*, 3-8.