Supplementary information

Synthetic strategies to incorporate Ru-terpyridyl water oxidation catalysts into MOFs: direct synthesis *vs.* post-synthetic approach

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Materials and Methods

Solvents

Methanol: gradient grade, VWR. Ethanol: absolute, VWR. Dichloromethane: stabilized (0.1% ethanol), >99%, VWR. Dimethylformamide: anhydrous, 99.8%, Sigma. Dimethylacetamide: ReagentPlus grade, ≥99%, Aldrich. Tetrahydrofurane: stabilized (BHT), ≥99%, VWR (Acros Organics). Dimethylsulphoxide-d6: >99.8%, Fluorochem.

Chemicals

Isonicotinic acid: 99%, Alfa Aesar. ZrOCl₂·8H₂O: puriss. p.a., ≥99.5%, Sigma. Triethylamine: synthesis grade, Merck. KH₂PO₄: ≥99%, Sigma. KOH: EMSURE grade, Merck. Multi-walled carbon nanotubes: NC7000[™], NANOCYL. HNO₃: NORMATOM grade, 67%, Sigma. H₂SO₄: ACS reagent grade, 95-98%, Sigma. H₂O₂: NORMAPUR grade, 30%, VWR. HF: 48%/H₂O, ≥99.99% (trace metals basis), Sigma. Formic acid: puriss., 98-100%, Merck.

NMR

¹HNMR analysis was performed with JEOL Resonance 400 MHz spectrometer (400YH magnet).

PXRD

Powder X-ray diffraction patterns (PXRD) were obtained using a Siemens D5000 diffractometer (Cu K α , λ =0.15418 nm) at 45 kV and 40 mA, using a step size of 0.02°.

SEM

MOF powders were sputter-coated with Au/Pd alloy prior to SEM experiments using Polaron SC7640 Sputter Coater (2 kV, 20 seconds). This helped avoid charge accumulation-related artefacts.

Scanning electron microscopy was performed on Carl Zeiss 1530 and 1550 SEM with InLens detector using 4.6 kV acceleration voltage.

BET

MOF samples were activated prior to measurement under dynamic vacuum at 80°C (down to $1x10^{-4}$ Pa) using a Micromeritic SmartVacPrep sample preparation unit.

Masses of MOFs used for BET analysis: 29 mg (MOF 3), 55 mg (MOF 4), 21 mg (MOF 5), 26 mg (MOF 6).

The N_2 sorption isotherms were recorded at 77 K using a Micromeritics ASAP 2060 instrument.

The BET surface area reported was calculated by the proprietary ASAP software.

ICP

ICP analysis was performed with Perkin Elmer Avio 200 ICP-OES system.

Electrochemical analysis

Electrode preparation: First, a stock suspension of multi-walled carbon nanotubes (MWCNT) was prepared by mixing the nanotubes with THF in the proportion 1mg/1mL and sonicating for 1 hour. Second, 1 mg of a MOF was added to 500 μ L of the MWCNT suspension and sonicated for 30 seconds to disperse the MOF crystals. Third, the GC surface was cleaned by two-step polishing with alumina (0,3 μ m followed by 0,05 μ m) with sonication in water and ethanol (3 min each) after each polishing step. Finally, the MOF/MWCNT suspension was dropcasted on the GC surface in 3 portions of 5 μ L each, allowing the electrode to dry between additions. A SEM micrograph of the produced electrode is presented in Figure S1. The electrochemical response was measured with several batches of each material and the behaviour was found qualitatively identical, with slight variations in current densities due to inexact weighting of the MOF and different degrees of contact between the MOF crystals and the carbon nanotubes.

Electrode setup: Ag/AgCl reference electrode, GC counter-electrode Buffer solution: pH 7.0 Phosphate buffer (43mM), ionic strength 0,1M Scanning rate: 0,1 V/s



Figure S1. SEM micrograph of MWCNT:edba-MOF 4 interface

Synthesis & Characterization

Ru(tda)(PyCO₂H)₂

The precursor complex and tda ligand were synthesized according to previously published procedures[1]. [Ru^{II}(k-N³O-tda)(dmso)(OH₂)] (100 mg, 0.2 mmol) and PyCOOH (200 mg, 1.6 mmol) were degassed and suspended in 25 mL of degassed water. The resulting suspension was heated up to reflux for one day. The starting insoluble solids dissolved at approximately 60 °C. At the end of the reaction, a little amount of red solid was observed, but it was not isolated. Instead, the resulting deep red reaction mixture was extracted with a mixture of DCM:Et₃N (50 mL:0.3 mL), and then with pure DCM. Then, the volume of the bulk aqueous layer was reduced to approximately 5 mL and an excess of pHO aqueous sulfuric acid was added. The red precipitate formed was filtered off, washed with ice-cold water and dried under vacuum (110 mg, 0.17mmol, 85 % yield). ¹HNMR (400 MHz, DMSO-*d*₆) δ 8.77 (2H, d, *J* = 8.2 Hz), 8.62 (2H, d, J = 7.7 Hz), 8.21 (4H, d, J = 6.0 Hz), 8.14 (1H, t, J = 8.1 Hz), 8.01 (2H, t, J = 7.8 Hz), 7.94 (2H, d, J = 7.9 Hz), 7.44 (4H, d, J = 6.7 Hz). ¹³CNMR (126 MHz, MeOD) δ 171.50, 169.73, 162.59, 158.53, 157.81, 152.73, 146.49, 136.98, 132.81, 127.03, 124.28, 124.15, 124.06. ESI⁻ HRMS m/z: calc. for (C₂₉H₁₈N₅O₈Ru⁻): 660.0237, found m/z: 660.0259 (3.3 ppm error). Anal. Calc. for C30H24N5O12RuS (compound + H₂SO₄ +CH₃OH +0.1 Et₃NH): C, 46.22 %; H, 3.10 %; N, 8.98 %; S, 4.11 %. Found: C, 46.22 %; H, 2.97 %; N, 9.14 %; S, 4.09 %.





Figure S2. (Top)¹HNMR spectrum of obtained Ru(tda)(PyCO₂H)₂. ¹HNMR (400 MHz, DMSOd₆) δ 8.77 (2H, d, J = 8.2 Hz), 8.62 (2H, d, J = 7.7 Hz), 8.21 (4H, d, J = 6.0 Hz), 8.14 (1H, t, J = 8.1 Hz), 8.01 (2H, t, J = 7.8 Hz), 7.94 (2H, d, J = 7.9 Hz), 7.44 (4H, d, J = 6.7 Hz). (Bottom) ¹³CNMR spectrum of Ru(tda)(PyCO₂H)₂. ¹³CNMR (126 MHz, MeOD) δ 171.50, 169.73, 162.59, 158.53, 157.81, 152.73, 146.49, 136.98, 132.81, 127.03, 124.28, 124.15, 124.06.

4,4'-Ethynedibenzoic acid (edba)

Edba was synthesized according to a published procedure[2]. ¹HNMR and ¹³CNMR spectra are presented in Figure S3.





Figure S3. (Top) ¹HNMR spectrum of edba. ¹HNMR (400 MHz, DMSO- d_6) δ 7.95 (d, J = 8.6 Hz), 7.67 (d, J = 8.6 Hz). (Bottom) ¹³CNMR spectrum of edba. ¹³CNMR (101 MHz, DMSO- d_6) δ 167.19, 132.26, 131.50, 130.14, 126.57.

Materials 1 & 2

The direct solvothermal synthesis procedure (material 1): $Ru(tda)(PyCO_2H)_2$ was mixed with $ZrOCl_2(H_2O)_8$ in a 1:1 molar ratio in DMA (38 µmol/3 mL), and 10x molar excess of formic acid was added (acetic acid and benzoic acid modulators have been tried as well). The mixture was then sonicated for 1 h, sealed in a vial and incubated in an oven between 80°C and 120°C for 2 days. The dark-red solid material was then separated from the liquid by centrifugation and washed using the standard washing procedure (see hereafter).

The 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.

The solvothermal co-synthesis procedure (material 2): $Ru(tda)(PyCO_2H)_2$, edba and $ZrOCl_2(H_2O)_8$ were mixed in a 1:1:2 molar ratio in DMA (38 µmol $ZrOCl_2(H_2O)_8/3$ mL), and 10x molar excess of formic acid was added. Other ratios between the linkers were tested as well (Figure S4). The mixture was sonicated for 1 h, sealed in a vial and incubated in an oven between 80°C and 120°C for 2 days. The dark-red solid material was then separated from the liquid by centrifugation and washed using the standard washing procedure.



Figure S4. PXRD patterns of materials with corresponding molar ratios of colinkers Ru(tda)(PyCO₂H)₂:edba.

Edba-MOF 3 and 4.

Edba (38 μ mol) and ZrOCl₂(H₂O)₈ (38 μ mol) were mixed in DMA (3 mL), in a 1:1 molar ratio, and 10x molar excess of formic acid (modulator) was added. The mixture was then sonicated for 1 h, sealed in a vial and incubated in an oven at 135°C for 2 days. The precipitate was separated by centrifugation and subjected to the standard washing procedure.

To selectively prepare octahedral MOF **3** (Figure S5A), 57 μ mol edba was mixed with 38 μ mol ZrOCl₂(H₂O)₈ in 3mL DMA, and 10x molar excess of formic acid (modulator) was added. The mixture was then sonicated for 1 h, sealed in a vial and incubated in an oven at 135°C for 2 days. The precipitate was separated by centrifugation and subjected to the standard washing procedure.

To selectively prepare interlaced MOF **4** (Figure S5B), 38 μ mol edba was mixed with 57 μ mol ZrOCl₂(H₂O)₈ in 3mL DMA, and 10x molar excess of formic acid (modulator) was added. The mixture was then sonicated for 1 h, sealed in a vial and incubated in an oven at 135°C for 2 days. The precipitate was separated by centrifugation and subjected to the standard washing procedure.



Figure S5. SEM images of edba-MOF synthesized with controlled excess of one of the components. (A) edba-MOF **3**, resulting from synthesis with 50% excess of edba. (B) edba-MOF **4**, resulting from synthesis with 50% excess of ZrOCl₂(H₂O)₈.

MOF 5 and 6

10 mg of MOF **3** or MOF **4** were pre-evacuated overnight prior to PSE. Then the powder was introduced into 3mL 5mM methanolic solution of Ru(tda)(PyCO₂H)₂ and the mixture was incubated at room temperature on shaker for 24 hours. Following centrifugal separation, the solid phase was subjected to 5 to 7 washing cycles with EtOH. The completion of washing procedure was confirmed by disappearance of Ru(tda)(PyCO₂H)₂ features in UV-Vis spectra of the supernatant. Subjected to this procedure, MOF **3** yielded MOF **5** and MOF **4** yielded MOF **6**.

PSE extent assessment: ICP

MOF digestion prior to ICP analysis: 5 mg of MOF were added to 4 mL of 3:1 HNO₃(67% NORMATOM grade):H₂O₂(30%) mixture, sealed and microwaved for 1 hour at 100°C. A dilution series using ICP grade water was prepared to choose the optimal concentration for ICP measurement.

Raw obtained data, each value averaged over 3 measurements, and corresponding molar concentrations are summarized in Table S1.

Ru-edba MOF 5	Zr	21,36 mg/L	0,234 mmol/L
	Ru	1,045 mg/L	0,0103 mmol/L
Ru-edba MOF 6	Zr	18,39 mg/L	0,2016 mmol/L
	Ru	0,452 mg/L	0,00447 mmol/L

Table S1. ICP data for calculation of PSE yield

Dividing them gives atomic ratios. For Ru-edba MOF **5**, Zr:Ru \cong 23. For Ru-edba MOF **6**, Zr:Ru \cong 45. The formula of the ideal UiO framework is $Zr_6O_4(OH)_4(linker)_6$, counting one zirconium atom per linker. Thus, assuming ideal stoichiometry, a 100% PSE yield would correspond to 1:1 Zr:Ru ratio. Then the obtained atomic ratios correspond to 4,2% apparent PSE yield for Ru-edba MOF **5** and 2,2% for Ru-edba MOF **6**.

PSE extent assessment: NMR

MOF digestion prior to NMR measurement: 5 mg of MOF was suspended in deuterated DMSO, 5 μ L of 48% HF was added and the mixture was sealed. The suspension was agitated until the MOF was completely dissolved.

The resulting spectra are presented in Figure S6. They differ from simple combination of edba and Ru(tda)(PyCO₂H)₂ signals likely due to degradation of the complex under the digestion conditions. However, clear signals of isonicotinic acid and edba can be isolated and used for quantification. The doublet at 7.5ppm corresponds to two out of four protons of isonicotinic acid (the other two are part of the 8.1ppm multiplet). The doublets at 7.65ppm and 7.95ppm correspond to edba. Ru(tda)(PyCO₂H)₂ bears two axial isonicotnic acid ligands, hence the 4H integral of the 7.5ppm doublet corresponds to one equivalent of the complex. Analogously, one equivalent of edba corresponds to two 4H doublets. In our calculations, the isonicotinic acid doublet integral is kept at 4H for reference and the resulting edba integrals are divided by 4 to yield the edba:Ru(tda)(PyCO₂H)₂ ratio. Thus, for Ru-edba MOF **5**, $\frac{119}{4} \cong 30$, and for Ru-edba MOF 6 $\frac{187}{4} \cong 47$. In other words, Ru-edba MOF 5 bears 30 edba linkers per one metallolinker, and Ru-edba MOF **6** has 47 edba linkers per one metallolinker. This corresponds to 3.2% and 2.1%, respectively. Assuming ideal UiO stoichiometry (no missing-linker defects), these percentages correspond to the apparent PSE yield.



Figure S6. ¹HNMR spectra of digested Ru-edba MOF 5 and Ru-edba MOF 6 with integrations.

Additional figures



Figure S7. (A) CV of MOF **5** compared to linker in solution; (B) CV of MOF **5** compared to pristine edba-MOF **3**; (C) CV of MOF **5** compared to MOF **6**. All measurements were performed vs Ag/AgCl reference electrode with GC counter-electrode, at scanning rate 0,1 V/s. Buffer solution: pH 7.0 Phosphate buffer (43mM), ionic strength 0,1M.



Figure S8. Variations in crystal morphology of edba-MOF. The images are adjusted to the same length scale.



Figure S9. PXRD patterns of edba-MOF before and after PSE. (A) pristine octahedral edba-MOF **3** vs Ru-MOF **5**. (B) pristine interlaced edba-MOF **4** vs Ru-MOF **6**.



Figure S10. CV study of the MOF resilience toward leaching in different ink suspensions performed by measuring voltammetric response of the ink before and after the MOF is removed by centrifugation. (A) Ethanolic suspension of Nafion and mesoporous carbon (carbon black, CB) retain intense ruthenium waves after the redox-active MOF is removed, demonstrating leaching of the Ru(tda)(PyCO₂H)₂ into the solution. (B) THF suspension of MWCNT does not retain the ruthenium redox features upon MOF precipitation, demonstrating that no measurable amount of Ru(tda)(PyCO₂H)₂ is leached into the solution under these conditions, and the redox response indeed originates in the MOF. During the centrifugation, the corresponding conductive components (CB or MWCNT) precipitated together with the MOF, so their content was replenished before the next measurement.



Figure S11. Cyclic voltammograms of materials **1**, **2**, **5** and **6** over 10 scans, showing gradual degradation of MOF-CNT interface and potential detachment of MOF crystals from the electrode (from black to red). (A) CV of material **1**; (B) CV of co-synthesized material **2**; (C) CV of Ru-edba-MOF **5** (octahedral); (D) CV of Ru-edba-MOF **6** (interlaced).



Figure S12. SEM micrographs showing: (A) material 1; (B) material 2.



Figure S13. FTIR spectra of linkers (edba and Ru(tda)(PyCO₂H)₂, top) and MOFs 3–6.

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