Supporting Information

A Covalent Organic Framework for Cooperative Water Oxidation

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Section S1. Materials and Instrumentation

Materials

All chemicals and reagents were purchased from commercial suppliers and used without further purification unless noted otherwise. Column chromatography was performed on silica-gel (particle size 0.040–0.063 mm) with freshly distilled solvents as eluents. Size exclusion chromatography was conducted with SX-3 BioBeads and HPLC grade solvents (dichloromethane/methanol 9/1). Multi-walled carbon nanotubes (MWCNTs) in bulk with a purity of > 95 %, OD > 50 nm, length ~ 50 μm were obtained from HeJi, Inc., China. Glassy carbon plates (GCp, 20 × 10 × 0.18 mm) were purchased from HTW, Germany. For electrochemical experiments, highly pure water was obtained by filtration of distilled water through a nanopure Milli-Q water purification system. Ru(DMSO)$_4$Cl$_2$ and 2,2′-bipyridine-6,6′-dicarboxylic acid (bda)$_{2,3}$ were prepared according to reported literature procedures.

Instrumentation

$^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were recorded on a Avance-400 spectrometer (Bruker-Daltonics GmbH, Germany) operating at 400 MHz ($^1$H) or 100 MHz ($^{13}$C), with the residual protic solvent used as the internal standard. The chemical shifts (δ) are reported in parts per million (ppm).

High resolution mass spectra (HRMS) were recorded on an ESI micrOTOF focus spectrometer (Bruker Daltonic GmbH, Germany).

FT-IR spectra were recorded with FT/IR-4600 spectrometer (ATR-module). The solid powder sample was used for the measurement. The analysis was performed NETZSCH JUPITER ST 449C instrument equipped with a TASC NETZSCH 414/4 controller.

All electrochemical experiments were carried out on an IJ-Cambria CHI-730 potentiostat. Glassy carbon disk (GC, φ = 0.3 cm, S = 0.07 cm$^2$), Pt mesh and Hg/HgSO$_4$ (K$_2$SO$_4$ sat.) were used as working electrodes (WE), counter electrode (CE), and reference electrode (RE), respectively in CV and DPV experiments. All potentials were converted to normal hydrogen electrode (NHE) by adding 0.65 V to the measured potential. CV and DPV measurements were performed in a 20 mL glass vial. A self-made Teflon cap with three holes was applied to hold the electrodes in the same distance. Electrodes for cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were prepared by drop-casting the Ru(bda)-COF/polymer-CNT (10 wt% CNT) dispersed solution (1 mg/mL suspension in THF) onto the surface of the glassy carbon disk. The sequential dropping (20 μL × 5) of the suspension was performed. Each drop was added onto electrode after the complete drying of the previous drop.

For Powder X-ray diffraction (PXRD) measurements, solid samples were activated at 100 °C in vacuum to remove any residual solvent or moisture from the samples. Samples were placed on a silicon holder and measured with a Bruker Discover D8 powder diffractometer using Cu $K_a$ radiation (unsplit $K_{a1} + K_{a2}$ doublet, mean wavelength $\lambda = 154.19$ pm) at a power of 40 kV and 40 mA, a focusing Goebel mirror, and a 1.2 mm microfocus alignment. The scattered X-ray beam went through a receiving slit with a 7.5 mm opening, 2.5° axial Soller slit, and detection was performed with a LynxEye-1D-Detector (Bruker AXS) using the full detector range of 192
channels. Measurements were done in reflection geometry in a coupled 2θ/θ mode with a step size of 0.025° in 2θ and 0.8 s measurement time per step in the range of 2–35° (2θ). Data collection and processing were carried out with the software packages DIFFRAC.Suite and DIFFRAC.EVA 2.1 from Bruker (Karlsruhe, Germany).

Argon sorption isotherms were measured at 87.3 K, on a Micro-300 sorption device from 3P Instruments. The measuring temperature of 87.3 K was realized by means of a cryoTune from 3P Instruments.

Scanning electron microscopy images were recorded using a Zeiss Ultra Plus field emission scanning electron microscope equipped with GEMINI e-Beam column operated at 1 kV with an aperture size set to 30 µm to avoid excessive charging and radiation damage of the areas imaged. The sample was prepared by the drop-casting of a suspension of COF in THF onto silicon wafer. For the energy dispersive X-ray analysis (EDX), the Oxford X-Max EDX detector and an accelerating voltage of 10 kV (aperture size was set to 120 µm) were used.

X-ray photoelectron spectroscopy was performed at the chair of experimental physics IV at Physikalisches Institut, Julius-Maximilians-Universität Würzburg (Germany). Sample powder was attached to a stainless steel Omicron flag style sample holder via carbon tape, and data was collected in a chamber pressure better than ~10⁻⁹ mbar using a monochromatized 1486.6 eV Al Kα photon source and an Omicron EA-135 analyser.

Methods

Synthesis of COF
The COF was synthesized by reacting tetra-(4-anilyl)methane (5.7 mg, 0.015 mmol) with Ru(bda)-aldehyde (16.5 mg, 0.03 mmol) in presence of 5 mL N,N-dimethylacetamide (DMAc) and mesitylene solvent combination (1:1). The reactants were taken in a 15 mL glass vial and ultrasonicated for 30 minutes in order to make a homogeneous solution. Then; the mixture was kept undisturbed inside of a preheated oven at 60 °C for 96 h. The solid precipitate was washed with DMAc for multiple times (4-5 times) until additional DMAc does not produce any coloured solution. The mixture was further treated with anhydrous dioxane for three times followed by vacuum drying to result a crystalline COF (Yield: ~55%).

Electrochemical Measurements
Electrochemical Measurements of as-synthesized Ru(bda)-COF/polymer were performed with 10 wt% multi-walled carbon nanotubes (MWCNTs) considering their poor electrical conductivity. Firstly, MWCNT (1 mg) was sonicated in THF (1 mL) for 45 min. The freshly prepared dispersion of MWCNTs in THF (0.2 mg in 0.2 mL) was added to a glass vial containing a suspension of Ru(bda)-COF/polymer (2 mg in 1.8 mL THF). The mixture was again sonicated for another 15 minutes for proper mixing. Then, this mixture was used for the electrode preparation.

Electrodes for cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were prepared by drop-casting the Ru(bda)-COF/polymer-CNT (10 wt% CNT) dispersed solution (1 mg/mL suspension in THF) onto the surface of the glassy carbon disk. The sequential dropping (20 µL × 5) of the suspension was performed. Each drop was added onto electrode after the complete drying of the previous drop. All the measurements were performed in 1 (M) phosphate buffers (pH = 7). The buffer was prepared by dissolving different amounts of phosphate salts in
highly pure Mili-Q water: pH 7, 1 M ionic strength: NaH$_2$PO$_4$ (23.1 g, 193 mmol) and Na$_2$HPO$_4$ (37.7 g, 266 mmol) in water (1000 mL).
For CV experiments, the scan rate was 100 mV/s unless stated otherwise. iR compensation at 85 % was applied for single CV and DPV experiments. Parameters in the DPV experiments were: ΔE = 4 mV, amplitude = 50 mV, pulse width = 0.05 s, sampling width = 0.0167 s and pulse period = 0.5 s.

Chemically driven water oxidation
The chemically driven water oxidation reactions were performed under ambient conditions in Schlenk reaction vessels, which were connected to pressure sensors from Honeywell (SSCDANN030PAAA5, absolute pressure, 0 to 30 psi). For each standard measurement, 1 g (1.82 mmol) of Cerium(IV) ammonium nitrate (CAN) was dissolved in 3 mL of a water (pH = 1, acid: trifluoromethane sulfonic acid, ratios varying) in a Schlenk flask with ultra-sonication. The dispersed catalyst solutions of various concentrations (400 μL in water (pH = 7, Mili-Q water)) were injected through a septum via a Hamilton syringe. Then, after certain time when there is no oxygen evolution (the curve gets flatten), the number of moles of oxygen evolution was calculated.

Initially, Ru(bda)-COF/polymer was sonicated in 1 mL water (pH = 7, Mili-Q water) in a 4 mL vial followed by stirring until a uniformly dispersed solution is resulted. The dispersed solution was used as stock solution for the catalysis. The stock was diluted further to prepare the lower concentrations of catalyst solution.

Photocatalytic water oxidation
The light-driven water oxidation reactions were carried out in an Oxygraph Plus System of Hansatech Instruments Ltd. Irradiation of the sample with a 150 W xenon lamp by Newport equipped with a 380 nm cutoff filter and a water jacket to remove UV and IR radiation, respectively. The intensity with which the sample was irradiated was 270 mW/cm$^2$. Before the measurement all components (catalyst, [Ru(bpy)$_3$]Cl$_2$ x 6 H$_2$O and Na$_2$S$_2$O$_8$ were dissolved in 3:7 CH$_3$CN/phosphate buffer (pH = 7.2) solution in the dark ([catalyst] = varying). Afterwards the sample was transferred to the reaction chamber and kept in the dark. After the baseline of the measurement was constant, the sample was irradiated (at the 50$^{th}$ second). During the measurement, the reaction temperature (20 °C) and stirring speed (100 rpm) were kept constant.

Kinetic isotope effect experiments
The kinetic isotope effect experiments were carried out in an Oxygraph Plus System of Hansatech Instruments Ltd. (Clark-type oxygen electrode for electrochemical oxygen detection; more details of the Oxygraph Plus System could be obtained from the Web site of Hansatech Instruments Ltd.). 1.5 mL of a freshly prepared CAN solution (c = 0.7 M, pH 1 solution (H$_2$O or D$_2$O with CF$_3$SO$_2$H)) was placed in the Clark electrode reaction chamber. 0.5 mL of the dispersed catalyst solution of Ru(bda)-COF/polymer (varying concentrations) were added after 25 seconds. During the measurement, the reaction temperature (20 °C) and stirring speed (100 rpm) were kept constant.

For the error estimation, the preparation of the individual solutions using Eppendorf pipettes and the catalyst injection by a Hamilton syringe (pressure sensor setup) or an Eppendorf pipette (Clark-electrode) was assumed to be the largest error sources. During chemical water oxidation, the error also appears due to the irregular dispersibility at higher concentration of 4 g L$^{-1}$. At very low concentration, the error also comes from the pressure sensors. The error bars are represented as standard deviation from the average value (3 times) without considering additional instrumental errors.
Section S2. Synthesis of molecular building block and WOCs

Synthesis of Ru(bda)-dialdehyde 1
Ru(bda)(DMSO)$_2$ 3 was synthesized following a previously reported protocol.\textsuperscript{4} 180 mg (0.365 mmol) of Ru(bda)(DMSO)$_2$ and excess pyridine-4-carboxaldehyde (386 mg, 3.6 mmol) were taken in a Schlenk flask and then kept under vacuum for 30 minutes. Afterwards, a mixture of degassed methanol and chloroform (1:1, 120 mL) was added. The mixture was degassed again for 30 minutes. Then the mixture was refluxed for 48 h. The solvents were evaporated, and the solid product was purified by column chromatography over aluminium oxide with 8% MeOH in CH$_2$Cl$_2$ as eluent. (isolated amount = 80 mg, isolated yield = 40%)

$^1$H NMR (400 MHz, MeOD, 298 K): δ = 8.58 (d, J = 8.2 Hz, 2H), 7.99 (d, J = 7.6 Hz, 2H), 7.87 (t, J = 7.8 Hz, 2H), 7.80 (d, J = 5.4 Hz, 4H), 7.25 (d, J = 6.4 Hz, 4H) ppm. $^{13}$C NMR (100 MHz, MeOD, 298 K): δ = 173.7, 160.1, 155.9, 151.7, 151.2, 131.8, 125.7, 125.0, 122.2, 94.7 ppm. HRMS (ESI-TOF, positive mode, MeCN/CH$_2$Cl$_2$): calcd for C$_{24}$H$_{16}$N$_4$O$_6$RuNa: 558.0108; found: 558.0115.

Scheme S1. Synthesis of Ru(bda)-dialdehyde 1.
Synthesis of Ru(bda)-polymer
Amorphous Ru(bda)-polymer was synthesized by imine condensation reaction of tetra-(4-anilyl)methane 2 (5.7 mg, 0.015 mmol) with Ru(bda)-dialdehyde 1 (16.5 mg, 0.03 mmol) in N,N-dimethylacetamide (DMAc, 5 mL). Both reactants were dissolved in DMAc in a glass vial and ultra-sonicated for 30 minutes to obtain a homogeneous solution. Afterwards, the vial was capped and kept in preheated oven at 120 °C for three days. Finally, the precipitated polymer was filtrated and washed with DMAc (10 mL, 3 to 5 times) to remove any residues of the starting materials. The collected deep reddish material was filtered and treated with THF for three times. The obtained powder was dried at 70 °C for eight hours under vacuum to obtain amorphous Ru(bda)-polymer (Yield: ~75%).

Scheme S2. Synthesis of Ru(bda)-polymer.
Synthesis of Ru(bda)-COF

The COF was synthesized by reacting tetra-(4-anilyl)methane 2 (5.7 mg, 0.015 mmol) with Ru(bda)-aldehyde 1 (16.5 mg, 0.03 mmol) in 5 mL N,N-dimethylacetamide (DMAc) and mesitylene solvent mixture (1:1). The reactants were taken in a 15 mL glass vial and ultrasonicated for 30 mins in order to make a homogeneous solution. Then, the mixture was kept in the preheated oven at 60 °C for 96 hours. The precipitate was washed with DMAc for multiple times (4-5 times) until addition of DMAc did not produce any colour. Then, the mixture was treated with anhydrous dioxane for three times followed by vacuum drying before further characterization (Yield: ~55%).

Scheme S3. Synthesis of Ru(bda)-COF.
Synthesis of R(bda) diimine complex
The monomer was synthesized by taking Ru(bda)-aldehyde (200 μmol) and excess 4-tert-butylaniline (1 mmol) in a Schlenk flask in presence of catalytic amount acetic acid (10 μL). Afterwards, degassed methanol (10 mL) was added. The mixture was degassed again for 30 minutes. Then the mixture was refluxed for 24 h. The solvents were evaporated, and the solid product was purified by column chromatography over aluminium oxide with 3% MeOH in CH₂Cl₂ as eluent. (isolated yield = 83%).

Scheme S4. Synthesis of Ru(bda) diimine complex.
Table S1. Optimization of the reaction condition for COF synthesis.\textsuperscript{a}

| Solvent          | Equivalents | Reaction time (h) | Temperature (°C) | Product     | Crystallinity |
|------------------|-------------|------------------|-----------------|-------------|---------------|
| MeOH             | -           | 72               | 60              | No precipitate |               |
| Tetrahydrofuran  | -           | 72               | 60              | No precipitate |               |
| DMF              | -           | 72               | 120             | precipitate  | amorphous     |
| 1,4-Dioxane      | -           | 72               | 60              | precipitate  | amorphous     |
| DMSO             | -           | 72               | 120             | No precipitate |               |
| N,N-Dimethylacetamide | -     | 72               | 120             | precipitate  | amorphous     |
| DMAc 1,4-Dioxane | 1 1         | 72               | 120             | precipitate  | amorphous     |
| DMAc methanol    | 1 1         | 72               | 120             | precipitate  | amorphous     |
| DMAc Mes         | 1 1         | 72               | 120             | precipitate  | poor          |
| DMAc Mes         | 1 1         | 96               | 60              | precipitate  | high          |

\textsuperscript{a}Reaction conditions: tetra-(4-anilyl)methane 2 (5.7 mg, 0.015 mmol) with Ru(bda) dialdehyde 1 (16.5 mg, 0.03 mmol) were taken in a 15 mL glass vial in presence of 5 mL corresponding solvent.

Figure S1. \textsuperscript{1}H NMR (400 MHz, MeOD, rt) spectrum of dialdehyde 1.
Figure S2. $^{13}$C NMR (100 MHz, MeOD, rt) spectrum of dialdehyde 1.

Figure S3. HR-ESI mass spectrum of dialdehyde 1.
Figure S4. $^1$H NMR (400 MHz, MeOD, rt) spectrum of Ru(bda) diimine complex.
Additional note on COF synthesis

During imine condensation, different monomers and molecular fragments are formed as byproducts and some smaller fragments are detected in HR-ESI mass spectra of the solvent residue after COF reaction (Figure S9). To optimize the reaction temperature, COF synthesis was carried out at 120 °C, 90 °C, 60 °C and even at room temperature. For the reaction at 120 and 90 °C, initial formation of COF seeds is so fast that precipitation of mostly amorphous phases occurs within a couple of hours. Some crystalline COF domains are embedded with amorphous polymer after the completion of the reaction (Figure S9b). The broad baseline confirms the presence of amorphous polymer phases besides crystalline domains. To slow down the rate of reaction and to allow a more ordered and slower growth of crystalline COF seeds, the best result was obtained for reaction at 60 °C. In the case of reaction at room temperature, formation of very less crystalline domains and a kinetically controlled formation of amorphous polymers as the main product is observed (Figure S9b). We further compared the residue solvents for each of the reaction mentioned above at different temperatures. From the color of the solution, it was obvious that in case of 60 °C there was lesser oligomers formation, thus indicating the highest yield for COF formation (Figure S5). In all the aforementioned cases, the reaction was performed for 4 days in a 1:1 mixture of polar DMAc and nonpolar mesitylene. The thermodynamic and kinetic parameters (temperature, pressure, dilution, catalysts, and modulators) determine the growth of the crystalline phase by suppressing the amorphous phase. In case of Ru(bda)-COF the reaction propagates through direct crystallization process. Once the amorphous phase is formed, it does not convert to the crystalline phase. Thus, conversion of amorphous polymer in to crystalline COF is not possible (Figure S10).

Figure S5. Residue solvents after COF synthesis at different temperatures.
Section S3. Structural Characterization

Simulated DFT-optimized molecular structure of Ru(bda)-dialdehyde 1

Figure S6. Energy optimized structure of Ru(bda)-dialdehyde 1 after DFT calculation with CAM-B3LYP functional and Def2SVP as basis set. The large <O-Ru-O bond angle provides enough space for a seventh coordination site for water coordination in higher oxidation states.
Powder X-ray diffraction

**Figure S7.** Comparison of powder X-ray diffraction (PXRD) patterns for starting materials Ru(bda) dialdehyde 1 and tetrakis-(4-anilyl)methane 2 and Ru(bda)-COF. The COF material shows distinct reflections with respect to both starting materials.

**Figure S8.** Comparison of PXRD patterns for microcrystalline Ru(bda)-COF (red) and amorphous Ru(bda)-polymer (black).
Figure S9. a) HR-ESI mass spectrum of the solvent residue for COF reaction at 60 °C. b) Powder X-ray diffraction pattern of as-synthesized semi-crystalline COF with embedded polymer at various temperatures.

Figure S10. Comparison of powder X-ray diffraction patterns of amorphous polymer before and after recrystallization. After synthesizing the polymer, it was separated by filtration. Then the polymer was retreated with same solvent combination ($N,N$-dimethylacetamide:mesitylene = 1:1) used during COF synthesis for 4 days at 60 °C.
**Structure simulation**

Geometries of interpenetrated diamondoid COF (\textit{dia-Cn}) were generated using the Automatic Topological Generator for Framework Structures (AuToGraFS) and optimized using UFF4MOF. AuToGraFS generates structures without symmetry (i.e. in \textit{P}1 space group) and so, in order to validate the calculated structures against the PXRD, symmetric structures with a simplified Ru linker were generated, by removing the (bda) unit, which is expected to be disordered. \(a = b\) lattice parameters were scanned, while \(c\) was allowed to optimize. All cell angles were held fixed at 90.0\(^\circ\). Non-symmetric calculations were undertaken using the Amsterdam Modelling Suite, AMS, [AMS 2020, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.] and symmetric calculations were undertaken using AMS and the General Utility Lattice Program, GULP.\(^6\) Interpenetrated images were generated using \textit{CrystalMaker}\(^\circledR\) (www.crystalmaker.com). Geometry optimization was performed using Gaussian 16, Revision C.01.\(^7\)

For the simulation of the interpenetrated structure, we have first scanned the various unit cell parameters \(a\) by keeping \(c\) as constant (\(a = b\)) (Figure S11). From experimental powder X-ray diffraction, it is obvious that the unit cell parameter ‘\(a\)’ must be less than 20 Å as the first peak appears at 6.8 Å experimentally. For closer inspection, then the unit cell parameter ‘\(a\)’ was scanned from 18 to 20 with 0.5 Å interval. And it has been observed that \(a = 19\) produces the PXRD pattern which is the closest to the experimental one (Figure S12). Although there is a shift observed for the first peak position, next three peaks are very close. Thus, the parameters corresponding to \(a = 19\) Å (\(a = b = 19\) Å and \(c = 19.7\) Å) were chosen for further refinement (Figure S13). Then, various degrees of interpenetration (from \textit{dia-C4} to \textit{dia-C7}) were simulated and their corresponding PXRD patterns were compared with the experimental pattern of the COF. The result clearly reveals that our experimental PXRD pattern matches best with the \textit{dia-C5} interweaving structure (Figure S13). The simulated pattern was then further refined with Pawley refinement (Figure S14,15). The structural details have been included in Table S2.
Figure S11. Comparison of simulated powder X-ray diffraction patterns of dia-C5 interpenetrated structure with different unit cell parameter ‘a’ varying from 20-25 Å (where $a = b$ and $c = 19.7$ Å).

Figure S12. Comparison of simulated powder X-ray diffraction patterns of dia-C5 interpenetrated structure with different unit cell parameter ‘a’ varying from 18-20 Å (where $a = b$ and $c = 19.7$ Å). Black coloured powder x-ray diffraction pattern corresponds to the experimental PXRD pattern of COF.
Figure S13. Comparison of simulated powder X-ray diffraction patterns of various interpenetrated structures with the experimental PXRD pattern.

Figure S14. Pawley refinement of the simulated *dia*-C5 COF structure. TP_Ru_C5_COF_scan_a19_final represents the *dia*-C5 Ru(bda)-COF and Suk-pxrd signifies the experimental PXRD pattern of the as-synthesized COF. Refinement was conducted using Material Studio software (Accelrys, Material Studio Release Notes, Release 4.2, Accelrys Software, San Diego 2006).
Table S2. Fractional atomic coordinates for the unit cell of the refined \textit{dia}-C5 interpenetrated diamondoid structure.\textsuperscript{b}

\textbf{Ru(bda)-COF (Space group P1) $a = 18.3$ Å, $b = 19.0$ Å, $c = 20.1$ Å; $\alpha = 92.4^\circ$, $\beta = 89.6^\circ$, $\gamma = 87.3^\circ$}

| atoms   | x       | y       | z       | atoms     | x       | y       | z       | atoms   | x       | y       | z       |
|---------|---------|---------|---------|-----------|---------|---------|---------|----------|---------|---------|---------|
| C1      | 0.4929  | 0.7544  | 0.6236  | N15       | 0.97    | 0.62144 | 0.14228 | O14      | 0.6591  | 0.12456 | 0.6388  |
| C2      | 0.5156  | 0.6567  | 0.3053  | N16       | 0.98    | 0.93647 | 0.10967 | C203     | 0.7938  | 0.5      | 0.79201 |
| C3      | 0.4660  | 0.8690  | 0.3140  | C107      | 0.97    | 0.64617 | 0.07478 | O15      | 0.9160  | 0.2873  | 0.79712 |
| N1      | 0.4784  | 0.6324  | 0.3580  | C108      | 0.97    | 0.90531 | 0.04607 | O16      | 0.8639  | 0.30089 | 0.89848 |
| N2      | 0.5066  | 0.8837  | 0.3670  | C109      | 0.94    | 0.61675 | 0.02251 | C204     | 0.8165  | 0.22737 | 0.50156 |
| C4      | 0.4851  | 0.6501  | 0.4272  | C110      | 0.92    | 0.91457 | 0.9953  | C205     | 0.5101  | 0.63339 | 0.23001 |
| C5      | 0.4938  | 0.8707  | 0.4362  | C111      | 0.94    | 0.645   | 0.95727 | C206     | 0.5620  | 0.6538  | 0.18187 |
| C6      | 0.4346  | 0.6334  | 0.4743  | C112      | 0.02    | 0.87807 | 0.93518 | C207     | 0.4544  | 0.59432 | 0.2028  |
| C7      | 0.5451  | 0.8841  | 0.4829  | C113      | 0.03    | 0.72149 | 0.9902  | C208     | 0.5578  | 0.63453 | 0.11172 |
| C8      | 0.4390  | 0.6557  | 0.5411  | C114      | 0.91    | 0.8279  | 0.96899 | C209     | 0.4504  | 0.57943 | 0.13211 |
| C9      | 0.5415  | 0.8599  | 0.5485  | C115      | 0.02    | 0.70291 | 0.05572 | N33      | 0.5014  | 0.59806 | 0.08614 |
| C10     | 0.4988  | 0.6943  | 0.5663  | C116      | 0.91    | 0.8631  | 0.0297  | Ru5      | 0.4992  | 0.55342 | 0.977   |
| C11     | 0.4825  | 0.8201  | 0.5726  | C117      | 0.17    | 0.76949 | 0.50979 | N34      | 0.5979  | 0.50402 | 3.8E-4  |
| C12     | 0.4323  | 0.7461  | 0.6798  | C118      | 0.23    | 0.73999 | 0.49716 | N35      | 0.4630  | 0.45875 | 0.0253  |
| C13     | 0.5598  | 0.7583  | 0.6738  | C119      | 0.13    | 0.79457 | 0.45134 | N36      | 0.4970  | 0.50316 | 0.87049 |
| C14     | 0.4257  | 0.8191  | 0.5292  | H81       | 0.27    | 0.72162 | 0.53908 | C210     | 0.6587  | 0.52262 | 0.9757  |
| C15     | 0.5525  | 0.7016  | 0.5204  | C120      | 0.26    | 0.73504 | 0.42981 | C211     | 0.5903  | 0.4541  | 0.05397 |
| C16     | 0.4302  | 0.8414  | 0.4629  | C121      | 0.16    | 0.78748 | 0.38501 | C212     | 0.5163  | 0.43836 | 0.0735  |
| C17     | 0.5442  | 0.6860  | 0.4534  | N17       | 0.23    | 0.75669 | 0.37348 | C213     | 0.3958  | 0.44821 | 0.03574 |
| C18     | 0.359   | 0.7092  | 0.9337  | Ru1       | 0.27    | 0.74675 | 0.26537 | C214     | 0.4765  | 0.43446 | 0.86214 |
| C19     | 0.6884  | 0.7745  | 0.9194  | N18       | 0.22    | 0.6487  | 0.24745 | C215     | 0.5138  | 0.53991 | 0.81248 |
| N3      | 0.3563  | 0.7562  | 0.8838  | N19       | 0.18    | 0.78433 | 0.21477 | C216     | 0.7233  | 0.48694 | 5.6E-4  |
| N4      | 0.6703  | 0.7397  | 0.8620  | N20       | 0.31    | 0.7375  | 0.15537 | C217     | 0.6624  | 0.58028 | 0.92682 |
| C20     | 0.3759  | 0.7498  | 0.8151  | C122      | 0.23    | 0.58751 | 0.27206 | C218     | 0.6482  | 0.4248  | 0.08147 |
| C21     | 0.6370  | 0.7479  | 0.7988  | C123      | 0.17    | 0.65667 | 0.19036 | C219     | 0.4963  | 0.42748 | 0.1376  |
| C22     | 0.3723  | 0.8071  | 0.7733  | C124      | 0.16    | 0.72989 | 0.16683 | C220     | 0.3732  | 0.41974 | 0.10241 |
| C23     | 0.6338  | 0.6926  | 0.7545  | C125      | 0.17    | 0.85135 | 0.20056 | C221     | 0.3426  | 0.47943 | 0.9901  |
| C24     | 0.3987  | 0.8066  | 0.7084  | C126      | 0.31    | 0.79395 | 0.11197 | C222     | 0.4687  | 0.40312 | 0.79703 |
| C55 | 0.4191 | 0.3058 | 0.4705 | C152 | 0.17 | 0.27593 | 0.88122 | 0.47525 | 0.48716 |
|-----|---------|---------|---------|-------|-----|---------|---------|--------|--------|
| C56 | 0.5378 | 0.1855 | 0.4720 | C153 | 0.17 | 0.11722 | 0.85246 | 0.25353 | 0.44349 |
| C57 | 0.4224 | 0.3426 | 0.5305 | C154 | 0.21 | 0.02466 | 0.77896 | 0.12244 | 0.62611 |
| C58 | 0.5328 | 0.1495 | 0.5317 | C155 | 0.30 | 0.06279 | 0.69104 | 0.23722 | 0.61159 |
| C59 | 0.9870 | 0.2701 | 0.1256 | C156 | 0.37 | 0.17372 | 0.93128 | 0.02161 | 0.45817 |
| C60 | 0.0049 | 0.1624 | 0.8051 | C157 | 0.34 | 0.29439 | 0.94134 | 0.48234 | 0.88333 |
| C61 | 0.1169 | 0.4259 | 0.8447 | H100 | 0.32 | 0.3465  | 0.8465  | 0.42530 | 0.88832 |
| C62 | 0.8874 | 0.1999 | 0.2156 | C175 | 0.17 | 0.9181  | 0.1939  | 0.1999  | 0.91304 |
| C63 | 0.0566 | 0.4201 | 0.0094 | O5   | 0.28 | 0.36906 | 0.67044 | 0.43438 | 0.89764 |
| C64 | 0.9235 | 0.1814 | 0.0386 | C160 | 0.36 | 0.23203 | 0.97473 | 0.54714 | 0.03452 |
| C65 | 0.9701 | 0.1672 | 0.9256 | O6   | 0.24 | 0.46856 | 0.71608 | 0.55625 | 0.89874 |
| C66 | 0.0022 | 0.4275 | 0.9654 | C159 | 0.17 | 0.04233 | 0.83322 | 0.49874 | 0.90255 |
| C67 | 0.1981 | 0.1567 | 0.9727 | O7   | 0.34 | 0.11298 | 0.66355 | 0.50198 | 0.94543 |
| C68 | 0.0556 | 0.4201 | 0.0094 | O8   | 0.32 | 0.96969 | 0.68063 | 0.40869 | 0.00376 |
| C69 | 0.9242 | 0.2617 | 0.1800 | C164 | 0.68 | 0.77241 | 0.11519 | 0.49757 | 0.05424 |
| C70 | 0.0539 | 0.2619 | 0.1744 | C165 | 0.78 | 0.71859 | 0.06706 | 0.61539 | 0.03656 |
| C71 | 0.9301 | 0.3592 | 0.0438 | N25  | 0.75 | 0.74127 | 0.12446 | 0.51389 | 0.06451 |
| C72 | 0.0397 | 0.2194 | 0.0171 | Ru3  | 0.80 | 0.73017 | 0.23054 | 0.48725 | 0.95462 |
| C73 | 0.9360 | 0.4008 | 0.9872 | N26  | 0.72 | 0.78272 | 0.28355 | 0.28368 | 0.01967 |
| C74 | 0.0317 | 0.1997 | 0.9511 | N27  | 0.73 | 0.64534 | 0.25747 | 0.33648 | 0.94026 |
| C75 | 0.8322 | 0.2138 | 0.4278 | C166 | 0.72 | 0.72024 | 0.3388  | 0.36554 | 0.06179 |
| C76 | 0.1497 | 0.2299 | 0.4128 | C176 | 0.72 | 0.85524 | 0.29254 | 0.52148 | 0.05953 |
| C77 | 0.8271 | 0.2604 | 0.3748 | C167 | 0.69 | 0.7407  | 0.33587 | 0.64317 | 0.05635 |
| C78 | 0.1781 | 0.2321 | 0.3514 | C168 | 0.69 | 0.6637  | 0.31845 | 0.66300 | 0.00317 |
| C79 | 0.8506 | 0.2567 | 0.3071 | C169 | 0.73 | 0.58018 | 0.23654 | 0.51122 | 0.09603 |
| C80 | 0.1399 | 0.2406 | 0.2913 | C170 | 0.84 | 0.65342 | 0.37163 | 0.48178 | 0.98505 |
| C81 | 0.8514 | 0.3165 | 0.2682 | C171 | 0.85 | 0.77767 | 0.38059 | 0.29335 | 0.05164 |
| C82 | 0.1212 | 0.1851 | 0.2511 | C172 | 0.71 | 0.88558 | 0.35972 | 0.38794 | 0.89719 |
| C83 | 0.8874 | 0.3207 | 0.2078 | C173 | 0.76 | 0.8966  | 0.24301 | 0.27377 | 0.90317 |
| C84 | 0.081  | 0.1943 | 0.1937 | C174 | 0.69 | 0.7654  | 0.39964 | 0.59830 | 0.06197 |

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| C85 | 0.0765 | 0.3172 | 0.2134 | C176 | 0.70 | 0.52354 | 0.27319 | O28 | 0.7310 | 9.5E-4 | 0.00314 |
|-----|--------|--------|--------|------|------|---------|---------|-----|-------|-------|---------|
| C86 | 0.8822 | 0.1961 | 0.2771 | C177 | 0.79 | 0.5614 | 0.18522 | C270 | 0.4948 | 8.057 | 0.74021 |
| C87 | 0.1215 | 0.3086 | 0.2668 | C178 | 0.85 | 0.64661 | 0.45128 | C271 | 0.9796 | 8.94745 | 0.23915 |
| C88 | 0.9784 | 0.7575 | 0.8778 | C179 | 0.86 | 0.77279 | 0.45326 | C272 | 0.9717 | 9.00776 | 0.29918 |
| C89 | 0.1371 | 0.7775 | 0.5803 | C180 | 0.69 | 0.84176 | 0.4116 | C273 | 0.9967 | 4.01897 | 0.24903 |
| C90 | 0.8776 | 0.6992 | 0.5668 | O9 | 0.79 | 0.86987 | 0.18874 | C274 | 0.9777 | 9.93885 | 0.36455 |
| N13 | 0.1572 | 0.7492 | 0.6392 | O10 | 0.77 | 0.96626 | 0.25354 | C275 | 0.0012 | 4.04882 | 0.31555 |
| N14 | 0.8583 | 0.7430 | 0.6161 | C181 | 0.67 | 0.53843 | 0.33265 | N45 | 0.9907 | 9.00931 | 0.37297 |
| C91 | 0.1225 | 0.7546 | 0.7022 | O11 | 0.83 | 0.6095 | 0.1627 | Ru8 | 0.9910 | 2.06013 | 0.47812 |
| C92 | 0.8698 | 0.7368 | 0.6863 | O12 | 0.80 | 0.49509 | 0.17128 | N46 | 0.9593 | 9.96633 | 0.53073 |
| C93 | 0.1317 | 0.7063 | 0.7530 | C182 | 0.86 | 0.70826 | 0.48982 | N47 | 0.0915 | 9.01383 | 0.50153 |
| C94 | 0.8517 | 0.7906 | 0.7287 | C183 | 0.66 | 0.24738 | 0.00377 | N48 | 0.9905 | 4.10705 | 0.58571 |
| C95 | 0.0935 | 0.7093 | 0.8129 | C184 | 0.64 | 0.29505 | 0.95351 | C276 | 0.8926 | 8.95307 | 0.54142 |
| C96 | 0.8749 | 0.7940 | 0.7947 | C185 | 0.71 | 0.19737 | 0.98151 | C277 | 0.0128 | 4.95319 | 0.58113 |
| C97 | 0.0436 | 0.7645 | 0.8261 | C186 | 0.66 | 0.29408 | 0.88638 | C278 | 0.0861 | 4.97118 | 0.56093 |
| C98 | 0.9177 | 0.7399 | 0.8237 | C187 | 0.73 | 0.19657 | 0.91257 | C279 | 0.1508 | 2.04625 | 0.46969 |
| C99 | 0.9889 | 0.7011 | 0.9389 | N29 | 0.71 | 0.24543 | 0.86589 | C280 | 0.0501 | 4.13467 | 0.61395 |
| C100 | 0.9650 | 0.8281 | 0.9218 | Ru4 | 0.76 | 0.24583 | 0.75819 | C281 | 0.9346 | 8.09594 | 0.62873 |
| C101 | 0.9239 | 0.6805 | 0.7847 | N30 | 0.66 | 0.2913 | 0.71455 | C282 | 0.8708 | 2.92841 | 0.60963 |
| C102 | 0.0401 | 0.8153 | 0.7770 | N31 | 0.78 | 0.35636 | 0.7702 | C283 | 0.8385 | 3.97796 | 0.49347 |
| C103 | 0.9022 | 0.6777 | 0.7183 | N32 | 0.79 | 0.24159 | 0.6477 | C284 | 0.9926 | 2.94527 | 0.64563 |
| C104 | 0.0758 | 0.8101 | 0.7172 | C188 | 0.64 | 0.24802 | 0.66988 | C285 | 0.1451 | 4.94831 | 0.59166 |
| C105 | 0.89E-4 | 0.6534 | 0.5806 | C189 | 0.67 | 0.36617 | 0.70191 | C286 | 0.2167 | 8.9948 | 0.49909 |
| C106 | 0.9658 | 0.9124 | 0.5784 | C190 | 0.72 | 0.40213 | 0.74221 | C287 | 0.1510 | 2.06355 | 0.40583 |
| C202 | 0.6399 | 0.3431 | 0.5867 | C191 | 0.83 | 0.37851 | 0.80906 | C288 | 0.0539 | 8.15293 | 0.68396 |
| O13 | 0.6550 | 0.1522 | 0.7494 | C192 | 0.80 | 0.29961 | 0.60672 | C289 | 0.9367 | 7.11199 | 0.69958 |
| C200 | 0.8132 | 0.2935 | 0.5345 | C193 | 0.79 | 0.17744 | 0.61641 | C290 | 0.9180 | 4.93006 | 0.66019 |
| C201 | 0.8084 | 0.1694 | 0.5453 | C194 | 0.63 | 0.2741 | 0.59943 | O29 | 0.8566 | 0.01026 | 0.43754 |
| O32 | 0.2089 | 0.0700 | 0.3702 | C195 | 0.64 | 0.17199 | 0.68608 | O30 | 0.7714 | 4.97176 | 0.50828 |
| C292 | 0.9972 | 0.1412 | 0.7294 | C196 | 0.65 | 0.39288 | 0.64183 | C291 | 0.2138 | 3.95994 | 0.55802 |
| C199 | 0.8788 | 0.3261 | 0.8385 | C197 | 0.73 | 0.47227 | 0.75094 | O31 | 0.2089 | 3.07007 | 0.37014 |
| C198 | 0.8394 | 0.4532 | 0.8214 | | | | | | | | |

b Atomic coordinates: Protons have been omitted in the table for simplicity.
Figure S15. Simulated crystal structure of Ru(bda)-COF: a), b) and c) are the view of the asymmetric unit along the b-, a- and c-axis respectively.
Additional notes on structural simulation

1) During structural simulation, molecular dynamics have been further performed to check for the possibility of structural changes after interpenetration. Molecular dynamics (MD) was undertaken for a total of 50 ps using a model of dia-C5 (5-fold interpenetrated diamond topology) using UFF4MOF-II as implemented in AMS2021.207. After 20 ps of equilibration, 50 ps of MD was undertaken in the NVT ensemble using a time step of 0.25 fs. A Nose-Hoover chain thermostat was used to maintain a temperature of 300 K. From the dynamics, the lowest (low-energy frame: 317) and highest energy frames (high-energy frames: 239, 1994) were extracted, as they are expected to be the most geometrically distorted from the previously optimised structure (lowest pattern). From the PXRD patterns, it is evident that there is no significant change in the diffraction pattern. The only differences are in the relative intensity of the peaks at ~4.5, 9.3, 11.1, 14.6 degree (Figure S16). Thus, structural integrity is maintained over the framework backbone once the interpenetrated structure is formed.

Figure S16. Comparison of PXRD patterns for various structures extracted from the molecular dynamics simulation of dia-c5 Ru(bda)-COF. [High-energy frames: 239, 1994; Low-energy frame: 317 and Medium-energy frames: 832, 1634; JMU-1-dia_C5: simulated from original C5 Ru(bda)-COF structure].
2) The rotation of one bda-unit (bda = 2,2'-bipyridine-6,6'-dicarboxylate) has also been considered. It has been found that the rotation does not lead to any other structure, as PXRD pattern remains unaltered after 180-degree rotation of the unit (Figure S17). From the molecular packing, it has been observed that once COF is crystallized in a particular order, there is no opportunity of the (bda)-unit to rotate further due to the space constraint. Thus, disorder of the bda units could predominantly be generated during crystallization or packing process.

![Figure S17. Comparison of PXRD patterns of Ru(bda)-COF before (top) and after (bottom) 180° rotation of (bda)-unit.](image-url)
**IR spectroscopy**

The IR spectra shows the absence of amine N–H stretching frequency (3100-3400 cm\(^{-1}\)) and aldehyde C–H frequency (2920 cm\(^{-1}\)) that confirms the purity of the product. The generation of new peak at 1620 cm\(^{-1}\) also signifies the formation of the imine bonding. This is as per the previous literature reports.\(^8\)

**Figure S18.** Comparison of the IR spectra for starting materials dialdehyde 1 and tetrakisamine 2, and imine frameworks a, Ru(bda)-COF and b, Ru(bda)-polymer.
Thermogravimetric analysis (TGA)

Figure S19. TGA of the as-synthesized a, Ru(bda)-polymer and b, Ru(bda)-COF. 1st derivative of wt% vs temperature plot has been shown in Figure c and d for Ru(bda)-polymer and Ru(bda)-COF, respectively.
BET (Brunauer, Emmett and Teller) surface area measurement

Solid samples for both Ru(bda)-polymer and Ru(bda)-COF were activated under high vacuum at 80 °C for two hours. Argon sorption isotherms were measured at 87.3 K, on a Micro-300 sorption device from 3P Instruments. The measuring temperature of 87.3 K was realized by means of a cryoTune from 3P Instruments. Both materials did not show any significant porosity. The shape of the isotherms and the obtained BET surface areas of 30 and 139 m² g⁻¹ for Ru(bda)-COF and Ru(bda)-polymer, respectively, indicate that both materials are nonporous and the measured surface areas correlate to coverage of the interface for the nanoparticles. Interestingly, a higher value for amorphous Ru(bda)-polymer has been observed as compared to crystalline Ru(bda)-COF, indicating a higher surface roughness for the amorphous polymer.

Figure S20. Ar sorption isotherm at 87 K for a) Ru(bda)-polymer and b) Ru(bda)-COF.
Scanning Electron Microscopy (SEM)

For SEM analysis of Ru(bda)-COF, a sample was casted using THF as solvent. On larger length scale (> 10 μm), Ru(bda)-COF possesses sheet-like morphology (Figs. S21a–c). However, a detailed look (Figs. S21c-d) indicates that individual sheets are formed from smaller spherical particles. Ultra-sonication of Ru(bda)-COF samples in water for 15 minutes leads to a partial disruption of the sheets (Figs. S21e–h). However, for complete disruption into the constituent spherical particles (Figs. S21i–l), sonication of a water suspension for 30 minutes in ultrasonication bath is necessary. The assembly of the smaller nanospheres (< 250 nm) can also lead to the larger nanospheres of 1-1.5 μm upon settling down for 5-6 hours (Figure S21k). The smaller nanospheres can be separated through polymeric membrane filters (Figure S23).

![SEM images for as-synthesized Ru(bda)-COF.](image)

**Figure S21.** SEM images for as-synthesized Ru(bda)-COF.
**Figure S22.** EDX spectrum of crystalline solid for a) Ru(bda)-COF plate and b) Ru(bda)-COF sphere (inserted SEM images) demonstrated the presence of Ruthenium in the macro-structures.

**Figure S23.** SEM images for Ru(bda)-COF after 30 minutes ultra-sonication. The histogram diameter shows the distribution of different particle sizes.
**Figure S24.** SEM image of Ru(bda)-polymer. The observed thread-like morphology differs significantly from the as-synthesized Ru(bda)-COF where nm-sized spheres are observed.
Section S4. Redox properties

The electrochemical properties were investigated by cyclic and differential pulse voltammetry to check the various oxidation states of the Ru(bda) units within the framework system. Considering the poor electrical conductivity of the Ru(bda)-COF/polymer, we have deposited the WOCs on 10 wt% of multi-walled carbon nanotubes as described in the main manuscript.\(^9\) Electrochemical Measurements of as-synthesized Ru(bda)-COF/polymer were performed with 10 wt% multi-walled carbon nanotubes (MWCNTs) considering their poor electrical conductivity. Firstly, MWCNT (1 mg) was sonicated in THF (1 mL) for 45 min. The freshly prepared dispersion of MWCNTs in THF (0.2 mg in 0.2 mL) was added to a glass vial containing a suspension of Ru(bda)-COF/polymer (2 mg in 1.8 mL THF). The mixture was again sonicated for another 15 minutes for proper mixing. Then, this mixture was used for the electrode preparation. All the measurements were performed in 1 M phosphate buffer (pH = 7). The buffer was prepared by dissolving different amounts of phosphate salts in highly pure Mili-Q water: pH 7, 1 M ionic strength: NaH\(_2\)PO\(_4\) (23.1 g, 193 mmol) and Na\(_2\)HPO\(_4\) (37.7 g, 266 mmol) in water (1000 mL). For CV experiments, the scan rate was 100 mV/s unless stated otherwise. iR compensation at 85 % was applied for single CV and DPV experiments. Parameters in the DPV experiments were: \(\Delta E = 4\) mV, amplitude = 50 mV, pulse width = 0.05 s, sampling width = 0.0167 s and pulse period = 0.5 s.

Table S3. Summary of the redox properties for Ru(bda)-COF and Ru(bda)-polymer at pH = 7 at room temperature.\(^c\)

| Oxidation     | Ru(bda)-COF (V) | Ru(bda)-Polymer (V) |
|---------------|-----------------|---------------------|
| \(\text{Ru}^{2+/3+}\) | 0.67            | 0.69                |
| \(\text{Ru}^{3+/4+}\) | 0.89            | 0.93                |
| \(\text{Ru}^{4+/5+}\) | 1.08            | 1.12                |

\(^c\)These values are with respect to NHE.
Figure S25. Comparison of electronic properties between Ru(bda)-COF and Ru(bda)-polymer measured in 1 (M) Phosphate buffers (pH = 7). a, and c, Comparison of the cyclic voltammograms (scan rate: 100 mV s$^{-1}$) of Ru(bda)-COF and Ru(bda)-polymer respectively. b, and d, Comparison of the differential pulse voltammograms ($\Delta E = 4$ mV, amplitude = 50 mV, pulse width = 0.05 s, sampling width = 0.0167 s and pulse period = 0.5 s) of Ru(bda)-COF and Ru(bda)-polymer respectively. iR compensation at 85 % was applied for single CV and DPV experiments.
Figure S26. Supramolecular H-bonding interactions between different threads of the interpenetrated structure of Ru(bda)-COF as observed in the structural model derived from PXRD measurements. This lowering in oxidation potential might be attributed to the ordered nanostructure of the extended Ru(bda) domains, in which COOH units from bda linkers of neighbouring threads participate in weak hydrogen bonding.
Section S5. Chemically driven water oxidation

The chemically driven water oxidation reactions were performed under ambient conditions in Schlenk reaction vessels, which were connected to pressure sensors from Honeywell (SSCDANN030PAAA5, absolute pressure, 0 to 30 psi). For each standard measurement, 1 g (1.82 mmol) of cerium(IV) ammonium nitrate (CAN) was dissolved in 3 mL of a water (pH = 1, acid: trifluoromethane sulfonic acid, ratios varying) in a Schlenk flask with ultra-sonication. The dispersed catalyst solutions of various concentrations (400 μL in water (pH = 7, Mili-Q water)) were injected through a septum via a Hamilton syringe. Then, after certain time when there is no oxygen evolution (the curve gets flatten), the number of moles of oxygen evolution was calculated. Initially, Ru(bda)-COF/polymer was sonicated in 1 mL water (pH = 7, Mili-Q water) in a 4 mL vial followed by stirring until a uniformly dispersed solution is resulted. The dispersed solution was used as stock solution for the catalysis. The stock was diluted further to prepare the lower concentrations of catalyst solution.

Variation of concentration for sacrificial electron acceptor ceric ammonium nitrate (CAN)

To screen for the most suitable reaction conditions for chemical water oxidation and to evaluate catalyst stability, CAN concentration was varied while keeping the amount of COF catalyst constant. For each measurement, 1 g L⁻¹ of Ru(bda)-COF was thoroughly dispersed in water (pH = 7). Afterwards, varying amounts of CAN (see Table S4) were added, and oxygen evolution was measured by a pressure sensor.

Figure S27. Chemical water oxidation for Ru(bda)-COF (3.4 mL of a 1.0 g L⁻¹ aqueous solution at pH = 1 (CF₃SO₂H:H₂O), 20 °C, 1000 rpm stirring speed in 3.4 mL) in the presence of various concentrations of CAN as sacrificial oxidant. Before the measurement, Ru(bda)-COF was dispersed overnight in H₂O (pH = 7). Oxygen evolution was measured with a pressure sensor and the initial rate of catalysis as determined from the slope for the first two seconds of oxygen evolution versus time for each measurement.
Table S4. Chemical water oxidation catalysis for Ru(bda)-COF at varying concentrations of CAN.

| CAN amount (µmol) | Initial rate (µmol L⁻¹ s⁻¹) | TONd |
|-------------------|-------------------------------|------|
| 45.5e             | 1873                         | –    |
| 91.9              | 1947                         | 32   |
| 182.3             | 2129                         | 72   |
| 455.9             | 2005                         | 180  |
| 911.9             | 1559                         | 368  |
| **1829.9**        | **1206**                     | **733** |
| 3647.9            | 859                          | 1581 |

d0.4 mg COF was used for each batch of the measurement. Considering the molecular weight of the COF as 1459.435 g/mol, 0.274 mmol of COF was taken into consideration for TON calculation. The TON has been represented for each (per) mole of Ru center.
eIt is due to the very low oxygen evolution at lower CAN concentration of 45.5 µmol that we could not determine data for the oxygen amount vs time plot as it is close to the sensing limit of the instrument. However, we were successful to get the initial data for rate measurement.

Table S5. Comparison of initial rates for chemical water oxidation catalysis with Ru(bda)-COF and Ru(bda)-polymer.f

| Catalyst concentration (g L⁻¹) | Initial rate for Ru(bda)-COF (µmol L⁻¹ s⁻¹) | Initial rate for Ru(bda)-polymer (µmol L⁻¹ s⁻¹) |
|-------------------------------|---------------------------------------------|-----------------------------------------------|
| 4                             | **26644**                                   | 809                                           |
| 2                             | 7450                                        | 444                                           |
| 1                             | 1852.9                                      | 215                                           |
| 0.5                           | 647                                         | 71                                            |
| 0.25                          | 368                                         | 22                                            |
| 0.125                         | 68                                          | 6                                             |

fChemical water oxidation for Ru(bda)-COF/polymer (3.4 mL of aqueous solution at pH = 1 (CF₃SO₃H:H₂O), 20 °C, 1000 rpm stirring speed in 3.4 mL) in the presence of various concentrations of WOC using1830 µmol of CAN as sacrificial oxidant. Before the measurement, Ru(bda)-COF/polymer was ultrasonicated first for 30 minutes followed by dispersion in H₂O (pH = 7).
**Turnover number (TON) calculation**

During a complete conversion of starting units to the COF, the below suggested structure should be the repeating unit for the framework. Thus, this structure with the empirical formula $C_{73}H_{48}N_{12}O_8Ru_2$ and a molecular weight of 1423.378 g mol$^{-1}$ can be considered as the smallest molecular fragment for the diamond-like network. However, the molecular weight of COF would be integer multiple of the molecular weight of this fragment. So, the molar amount of COF we are using for the calculation purpose should be quite lower than our current consideration which should relate to higher catalytic activity.

To quantify the amount of Ru within the materials, we can define the smaller fragment $C_{36.5}H_{24}N_6O_4Ru$ and a molecular weight of 711.689 g mol$^{-1}$, which can be used to calculate the TON per individual Ru center for the as-synthesized COF.

During the chemical water oxidation, it has been observed that the catalytic performance of Ru(bda)-COF is only limited by the amount of CAN. Thus, considering the 5-cycle recyclability opportunities of the COF, five times of the TON for the individual catalytic cycle ($5 \times 576 = 2880$) should be a lower barrier for the intrinsic TON of Ru(bda)-COF (Figure S30b).

**Scheme S5.** Repeating unit responsible for network formation in COF.
Table S6. TON in chemical water oxidation for a single catalytic cycle.\(^g\)

| mmol amount of catalyst (mg) | Amount of O\(_2\) evolved in COF (mmol) | Amount of O\(_2\) evolved in polymer (mmol) | TON\(_{\text{COF}}\) (μmol/g) | TON\(_{\text{polymer}}\) (μmol/g) | TON\(_{\text{polymer}}\) (μmol/g) |
|-----------------------------|-----------------------------------------|------------------------------------------|-----------------------------|---------------------------------|---------------------------------|
| 0.00239 (0.5)              | 0.3970                                  | 0.3229                                   | 166                         | 794000                          | 135                            |
|                             |                                         |                                          |                             |                                 |                                 |
| 0.00119 (0.25)             | 0.3830                                  | 0.0769                                   | 321                         | 1532000                         | 64                             |
|                             |                                         |                                          |                             |                                 |                                 |
| 0.00060 (0.125)            | 0.3437                                  | 0.0179                                   | 576                         | 2749600                         | 30                             |

\(^g\)In order to follow the conventional way of TON calculation, the molar amount of Ru in Ru(bda)-COF and Ru(bda)-polymer was considered (see calculation of the adjusted molecular weight above). However, we have also considered a new way of representing the TON for heterogeneous system where TON (mol/g) is defined as the total amount of oxygen evolved per gram of WOC. The TON represented herein is only for single catalytic cycle for COF.

Figure S28. Determination of rate constants for water oxidation catalysis with Ru(bda)-COF (left) and Ru(bda)-polymer (right) from linear fits of initial rates at varying catalyst concentrations. The slope for the first two seconds of catalysis was used to determine the initial rate for the particular concentration of Ru(bda)-COF. For Ru(bda)-polymer, the initial rate for each catalyst concentration was calculated from the slope between 150-155 s considering the sigmoidal nature of the oxygen evolution curves. Linear regression fits determined the rate constants of the reactions (second order \(k_{\text{COF}} = 1655\ \mu\text{mol L}^{-1}\ \text{g}^{-1}\ \text{s}^{-1}\) for Ru(bda)-COF and first order \(k_{\text{polymer}} = 211\ \mu\text{mol g}^{-1}\ \text{s}^{-1}\) for Ru(bda)-polymer).
**Recyclability test**

To elaborate on the recyclability of heterogeneous Ru(bda)-COF, the catalyst was recovered and reused for further cycles multiple times. To demonstrate that there is no considerable decrease in catalytic performance, we have performed five consecutive catalytic cycles with one batch of Ru(bda)-COF catalyst. The facile recovery of the catalyst from the reaction solution by simple filtration is shown in Figure S29, as the COF is collected at the bottom of the reaction tube after the reaction. To avoid any degradation of the imine framework under highly acidic conditions, water oxidation catalysis was measured for five minutes followed by recovery of the catalyst from the reaction solution for the next cycle.

![Figure S29](image-url)

**Figure S29.** Recovery of Ru(bda)-COF catalyst from the reaction mixture. For recycling, the catalyst suspension was transferred to a new and centrifuged. The COF material was further washed with water multiple times to remove traces of CAN, if any, from the surface followed by drying in vacuum before the next cycle.

![Graphs](image-url)

**Figure S30.** Chemical water oxidation catalysis for recycled batches of Ru(bda)-COF (1.0 g L$^{-1}$ in 3.4 mL aqueous solution at pH = 1 (CF$_3$SO$_3$H:H$_2$O), 20 °C, CAN (1 g, 1.82 mmol) as sacrificial oxidant, 1000 rpm stirring speed). Before each cycle, Ru(bda)-COF was dispersed overnight in H$_2$O (pH = 7); a) oxygen evolution was measured with a pressure sensor and b) TON have been calculated based on the amount of Ru centers. As the catalyst is still active after 5 cycles the cumulative TON should be over 3100.
Figure S31. PXRD and IR spectra of Ru(bda)-COF before and after the catalysis. The measurements were performed after recollecting the COF material from the reaction tube and activation at 90 °C for ten hours in high vacuum.

Estimation of crystallite size

Crystallite size calculation using the Williamson-Hall (W–H) plot method has been performed considering a Gaussian fitting for the first four high intensity reflections in diffractograms for Ru(bda)-COF from the recycling experiments. This analysis suggests that the COF crystallite size does not alter considerably even after five catalytic cycles.

In XRD data, the total broadening ($\beta_T$) of the reflections is due to the broadening effect of crystallites size ($\beta_D$) and micro strain ($\beta_\varepsilon$).

$$\beta_T = \beta_D + \beta_\varepsilon$$

From Scherer equation, we know

$$D = \frac{K\lambda}{\beta_D \cos \theta}$$

Where $\beta_D$ is the FWHM in radians, $K = 0.9$ is the shape factor, $\lambda = 0.15406$ nm is the wavelength of the X-ray source, $D$ is the crystallite size and $\theta$ is the peak position in radian.

Again, the XRD broadening due to micro strain is given by,

$$\beta_\varepsilon = 4 \varepsilon \tan \theta$$

Thus, it could be written rearranging as

$$\beta_T \cos \theta = 4 \varepsilon \sin \theta + \frac{K\lambda}{D}$$

This equation is comparable as $y = mx + c$

Where $y = \beta_T \cos \theta$, $m = \varepsilon$, $x = 4\sin \theta$ and intercept $c = \frac{K\lambda}{D}$
Table S7. Crystallite size calculation from the FWHM of the first four reflections of the experimentally measured PXRD diffractogram for Ru(bda)-COF before the catalysis.

| Peak sequence (before catalysis) | 2θ (degree) | FWHM (β_T) | β_T cosθ | 4 sinθ |
|----------------------------------|-------------|------------|-----------|--------|
| 1.                               | 6.98312     | 0.40165    | 0.006997  | 0.243606 |
| 2.                               | 9.27349     | 0.40264    | 0.007004  | 0.323353 |
| 3.                               | 11.58705    | 0.36295    | 0.006302  | 0.403775 |
| 4.                               | 12.59782    | 0.29761    | 0.005163  | 0.438862 |

Figure S32. Beta cos(θ) vs 4 sin(θ) plot for Ru(bda)-COF before the catalysis. The linear fitting curve reveals an intercept value of 0.00804, which corresponds to a crystallite size of ~17 nm.
**Table S8.** Crystallite size calculation from the FWHM of the first four reflections of the experimentally measured PXRD diffractogram for Ru(bda)-COF after the 5th catalytic cycle.

| Peak sequence (after 5th catalysis) | 2θ (degree) | FWHM (βT) | βT cosθ | 4 sinθ |
|-------------------------------------|-------------|------------|---------|--------|
| 1.                                  | 6.96419     | 0.40601    | 0.007073 | 0.242946 |
| 2.                                  | 12.57394    | 0.31791    | 0.005515 | 0.438033 |
| 3.                                  | 11.52275    | 0.40032    | 0.006952 | 0.401542 |
| 4.                                  | 9.37715     | 0.33513    | 0.00583  | 0.326959 |

**Figure S33.** Beta cos(θ) vs 4 sin(θ) plot for Ru(bda)-COF after the 5th catalytic cycle. The linear fitting curve reveals an intercept value of 0.00804, which corresponds to a crystallite size of ~14 nm.
**Control experiment**

To rule out any decomposition of the heterogeneous catalyst and leakage of active Ru species as homogeneous catalysts, Ru(bda)-COF was ultra-sonicated for 30 minutes followed by stirring for 6 hrs in water and filtered afterwards. The filtrate was then tested in water oxidation catalysis. However, no evolution of O\textsubscript{2} was detected for 80 minutes, thus indicating the chemical integrity of Ru(bda)-COF in water, and ruling out any homogeneous phase reaction.

![Control experiment](image)

**Figure S34.** Control experiment for chemical water oxidation in the homogeneous aqueous phase. No O\textsubscript{2} evolution in the presence of CAN was observed for the filtrate of an aqueous Ru(bda)-COF suspension.

![EDX spectrum](image)

**Figure S35.** EDX spectrum of thin film prepared by drop-casting the filtrate after chemical water oxidation onto silicon wafer. The following chemical elements were detected: Carbon (C) at K\textalpha\(0.277\), Nitrogen (N) at K\textalpha\(0.392\), Oxygen (O) at K\textalpha\(0.525\), Fluorine (F) at K\textalpha\(0.677\), Cerium (Ce) at M\textalpha\(0.884\) and M\textalpha\(4.839\), Silicon (Si) at K\textalpha\(1.740\) (substrate!) and Sulphur (S) at K\textalpha\(2.309\). For the analysis, the Oxford X-Max EDX detector and an accelerating voltage of 10 kV (aperture size was set to 120 \textmu m) were used.
Section S6. Photocatalytic water oxidation

The light-driven water oxidation reactions were carried out in an Oxygraph Plus System of Hansatech Instruments Ltd. Irradiation of the sample with a 150 W xenon lamp by Newport equipped with a 380 nm cut-off filter and a water jacket to remove UV and IR radiation, respectively. The intensity with which the sample was irradiated was 270 mW/cm². Before the measurement all components (catalyst, [Ru(bpy)₃]Cl₂ x 6 H₂O and Na₂S₂O₈) were dissolved in 3:7 CH₃CN/phosphate buffer (pH = 7.2) solution in the dark ([catalyst] = varying). Afterwards the sample was transferred to the reaction chamber and kept in the dark. After the baseline of the measurement was constant, the sample was irradiated (at the 50th second). During the measurement, the reaction temperature (20 °C) and stirring speed (100 rpm) were kept constant.

Additional note on photocatalytic water oxidation

During photocatalytic water oxidation, the photosensitizer (PS) is excited to PS* in presence of light, which subsequentially is oxidized by the persulphate to PS⁺ (Figure S36a). This transient species further interacts with the WOC in the ground state in consecutive cycles to generate the highly oxidized Ru(V) state, which ultimately proceeds through I2M pathway and generates oxygen. Thus, photocatalytic activity is predominantly limited by the rate of generation of PS⁺. Alteration of the sensitizer could decrease the driving force for excited state oxidative quenching by the persulfate anion thereby affecting the overall catalytic activity. Even the hole-transfer process from photogenerated PS⁺ to the WOC could limit the catalysis. Herein, absorption and luminescence spectroscopy (quenching studies) have already been used to assess the energy states and the stability of PS.¹⁰ From cyclic and differential pulse voltammograms we have assigned the various oxidation potentials and provided the energy scheme of photocatalytic water oxidation (Figure S36b).
Figure S36. a) Catalytic cycle and b) Energy scheme for photocatalytic water oxidation with [Ru(bpy)_3]Cl_2 as photosensitizer, Na_2S_2O_8 as sacrificial electron acceptor and Ru(bda)-COF as WOC. The potential for the oxidation of water to molecular oxygen at pH 7 was calculated by the Nernst equation: E = 1.23 – (0.059 x pH) V vs. NHE. Oxidation potentials of the sensitizers was obtained from literature reference. Oxidation potentials of Na_2S_2O_8 were obtained from literature references.
Figure S37. Photocatalytic oxygen evolution curves for Ru(bda)-COF (2 mL of 0.07 g L⁻¹ solution in 1:1 MeCN/phosphate buffer (pH = 7), stirring speed 100 rpm, oxygen evolution was measured with a Clark-type electrode set-up) with varying concentrations of photosensitizer (Ru(bpy)₃Cl₂) and sacrificial electron acceptor (Na₂S₂O₈). Irradiation of the samples started at $t = 50$ s. Linear fitting of oxygen evolution curves between 65-75 seconds provided the initial rates.

Figure S38. Photocatalytic oxygen evolution curves for Ru(bda)-COF (0.07 g L⁻¹, stirring speed 100 rpm, $c$(Ru(bpy)₃Cl₂) = 1.66 mM, $c$(Na₂S₂O₈) = 41 mM, oxygen evolution was measured with a Clark-type electrode set-up) in different solvent mixtures of MeCN and phosphate buffer (pH = 7). Irradiation of the samples started at $t = 50$ s. Linear fitting of oxygen evolution curves between 55-70 seconds provided the initial rates.
Figure S39. Plots of initial photocatalytic water oxidation rates for Ru(bda)-COF against the square of COF concentration (a, left) and for Ru(bda)-polymer against the polymer concentration (b, right). Unlike for the chemical water oxidation, in photocatalysis no sigmoidal curve is observed for Ru(bda)-polymer, as there is presumably enough time for complete dispersion of the polymer before the start of the irradiation. Linear regression fits determined the rate constants of the reactions (second order $k_{\text{COF}} = 1072 \, \mu\text{mol L}^{-1}\text{s}^{-1}\text{g}^{-2}$ for Ru(bda)-COF and first order $k_{\text{polymer}} = 3 \, \mu\text{mol s}^{-1}\text{g}^{-1}$ for Ru(bda)-polymer).
Figure S40. Photochemical water oxidation catalysis for Ru(bda)-COF particles in the range of 0.5–1 μm. Photocatalytic oxygen evolution curves for varying amounts of Ru(bda)-COF (2 mL of 7:3 MeCN/phosphate buffer (pH = 7) solution, c(Ru(bpy)_3Cl_2) = 1.66 mM, c(Na_2S_2O_8) = 41 mM, oxygen evolution was measured with a Clark-type electrode set-up, irradiation of the samples started at t = 50 s). Linear fitting of oxygen evolution curves between 65-75 sec provided the initial rates. Plots of the initial rates versus the catalyst concentration with quadratic fit and versus square of catalyst concentration with corresponding linear regression fit determined the second order rate constant photocatalytic water oxidation for Ru(bda)-COF particles (k = 1169 μmol L s\(^{-1}\) g\(^{-2}\) for 0.5–1 μm particles). The as-synthesized COF was initially sonicated for 30 minutes to transform them into nano-spheres. Then, the spheres were settled down for 6 hours followed by separation of the smaller nano-spheres through membrane filtration (PES membrane cut off size = 450 nm). The large nano-spheres were collected back and used for catalysis.
Figure S41. Unimodal distribution in dynamic light scattering for Ru(bda)-COF in water: Mean = 850 nm; angle 90°, PI = ~0.7.
Photochemical water oxidation catalysis for Ru(bda)-COF particles with size < 500 nm. Photocatalytic oxygen evolution curves for varying amounts of Ru(bda)-3D-COF (2 mL of 7:3 MeCN/phosphate buffer (pH = 7) solution, $c$(Ru(bpy)$_3$Cl$_2$) = 1.66 mM, $c$(Na$_2$S$_2$O$_8$) = 41 mM, oxygen evolution was measured with a Clark-type electrode set-up, irradiation of the samples started at $t = 50$ s). Linear fitting of oxygen evolution curves between 65-75 sec provided the initial rates. Plots of the initial rates versus the catalyst concentration with quadratic fit and versus square of catalyst concentration with corresponding linear regression fit determined the second order rate constant photocatalytic water oxidation for Ru(bda)-3D-COF particles ($k = 1591 \mu$mol L s$^{-1}$ g$^{-2}$ for particles < 500 nm). The as-synthesized COF was initially sonicated for 30 minutes to transform them into nano-spheres. Then, the smaller nano-spheres were separated through filtration with polymeric membrane.
Figure S43. Unimodal distribution in dynamic light scattering for Ru(bda)-COF in water; Mean = ~375 nm; angle 64 and 90°, PI = -0.35.
Figure S44. a) Time-dependent O₂ evolution for various amounts of Ru(bda)-COF during photochemical water oxidation catalysis without any rotation. (2 mL solution of 7:3 MeCN/aqueous phosphate buffer (pH = 7), c([Ru(bpy)₃]Cl₂) = 1.66 mM, c(Na₂S₂O₈) = 41 mM, irradiation started at t = 50 s and O₂ formation was measured with a Clark-type electrode set-up). b) Plots of initial catalysis rates (obtained by linear fit of O₂ evolution curve between 145-155 s) versus WOC concentration with corresponding linear regression fit.

Table S9. Comparison of initial rates and rate constants for WOCs.

| measurements        | Ru(bda)-COF          | Ru(bda)-polymer       |
|---------------------|----------------------|-----------------------|
| chemical water      | initial rate         | 26644 µmol L⁻¹ s⁻¹    | 809 µmol L⁻¹ s⁻¹   |
| oxidation⁽ᵃ⁾        | rate constant        | 1655 µmol L⁻¹ s⁻²     | 211 µmol g⁻¹ s⁻¹  |
| photochemical       | initial rate         | 10.9 µmol L⁻¹ s⁻¹     | 0.5 µmol L⁻¹ s⁻¹  |
| water oxidation⁽ᵇ⁾ | rate constant        | 1591 µmol L⁻¹ s⁻²     | 3 µmol s⁻¹ g⁻¹   |

⁽ᵃ⁾The highest rate corresponds to WOCs concentration of 4 g L⁻¹. The initial catalysis rates versus WOC concentration with corresponding linear (Ru(bda)-polymer) and quadratic (Ru(bda)-COF) regression fit results the rate constant. ⁽ᵇ⁾The highest rate reported herein corresponds to the concentration of 0.08 g L⁻¹ and 0.1 g L⁻¹ for Ru(bda)-COF and Ru(bda)-polymer respectively.
Table S10. Comparison of photocatalytic activities in the best performing heterogeneous systems reported in the literature.

| Substrate               | Evolved gas | Rate constant | Rate (0.1 g L⁻¹) |
|-------------------------|-------------|---------------|------------------|
| TtaTfa¹⁴                | H₂          | 20700 μmol h⁻¹ g⁻¹ | 0.58 μmol L⁻¹ s⁻¹ |
| Ter-CTF-0.7¹⁵           | H₂          | 19120 μmol h⁻¹ g⁻¹ | 0.53 μmol L⁻¹ s⁻¹ |
| FS-COF¹⁶                | H₂          | 16300 μmol h⁻¹ g⁻¹ | 0.45 μmol L⁻¹ s⁻¹ |
| RuOx/CTF-1-100 W¹⁷      | O₂          | 140 μmol h⁻¹ g⁻¹ | 0.004 μmol L⁻¹ s⁻¹ |
| g-C40N3-COF¹⁸           | O₂          | 50 μmol h⁻¹ g⁻¹ | 0.001 μmol L⁻¹ s⁻¹ |
| Ru(bda)-COF             | O₂          | 1590 μmol L s⁻¹ g⁻² | 10.9 μmol L⁻¹ s⁻¹ |
| Ru(bda)-polymer         | O₂          | 10800 μmol L h⁻¹ g⁻¹ | 0.5 μmol L⁻¹ s⁻¹ |

Figure S45. Cartoon representation to illustrate the cooperative interaction in covalent organic framework during O–O bond formation. The periodic arrangements simultaneously bring multiple units together during the interaction of two metal centers on the surface.
Kinetic isotope effect measurements

The kinetic isotope effect experiments were carried out in an Oxygraph Plus System of Hansatech Instruments Ltd. (Clark-type oxygen electrode for electrochemical oxygen detection; more details of the Oxygraph Plus System could be obtained from the Web site of Hansatech Instruments Ltd.). 1.5 mL of a freshly prepared CAN solution (c = 0.7 M, pH 1 solution (H₂O or D₂O)) was placed in the Clark electrode reaction chamber. 0.5 mL of the dispersed catalyst solution of Ru(bda)-COF/polymer (varying concentrations) were added after 25 seconds. During the measurement, the reaction temperature (20 °C) and stirring speed (100 rpm) were kept constant.

*Figure S46.* Plot of initial catalyst rate versus catalyst concentration with linear regression fit for reactions of Ru(bda)-COF (left) and Ru(bda)-polymer (right) in H₂O (green) and D₂O (red) to determine \( k_{\text{H}_2\text{O}} \) and \( k_{\text{D}_2\text{O}} \) for estimation of the kinetic isotope effects.
Figure S47. Kinetic isotope effect measurements for Ru(bda) diimine complex. Time-dependent O₂ evolution during chemical water oxidation for various amounts of catalyst (2 mL of H₂O (solid lines) or D₂O (dashed lines) using CAN (0.53 M) as sacrificial oxidant, pH = 1, 20 °C, 100 rpm stirring speed, O₂ formation was measured with a Clark-type electrode set-up).

Figure S48. a) Plots of initial catalysis rates versus Ru(bda) diimine complex concentration. b) Plot of initial catalyst rate versus square of catalyst concentration with linear regression fit in H₂O (black) and D₂O (red) to determine $k_{H₂O}/k_{D₂O}$ for estimation of the kinetic isotope effects.
Figure S49. Kinetic isotope effect measurements for the Ru(bda)-aldehyde. Time-dependent O₂ evolution during chemical water oxidation for various amounts of catalyst (2 mL of H₂O (solid lines) or D₂O (dashed lines) using CAN (0.53 M) as sacrificial oxidant, pH = 1, 20 °C, 100 rpm stirring speed, O₂ formation was measured with a Clark-type electrode set-up).

Figure S50. a) Plots of initial catalysis rates versus Ru(bda)-aldehyde concentration. b) Plot of initial catalyst rate versus square of catalyst concentration with linear regression fit in H₂O (black) and D₂O (red) to determine k_{H₂O}/k_{D₂O} for estimation of the kinetic isotope effects.
Figure S51. a) Time-dependent O₂ evolution during chemical water oxidation for various amounts of Ru(bda)-COF (2 mL of H₂O (solid lines) or D₂O (dashed lines) using CAN (0.53 M) as sacrificial oxidant, pH = 1, 20 °C, without any stirring, O₂ formation was measured with a Clark-type electrode set-up). b) Plots of initial catalysis rates versus Ru(bda)-COF concentration (first order rate constants were determined by linear regression fit for plots of initial rates versus Ru(bda)-COF concentration.

\[ k_{\text{H₂O}} = 322.4 \text{ mmol g}^{-1} \text{s}^{-1} \]
\[ k_{\text{D₂O}} = 167.7 \text{ mmol g}^{-1} \text{s}^{-1} \]
\[ k_{\text{H₂O}} / k_{\text{D₂O}} = 1.92 \]
Comparison of activity for Ru(bda)-COF and molecular precursor Ru(bda) dialdehyde 1

Chemical water oxidation (3.4 mL aqueous solution at pH = 1 (CF$_3$SO$_3$H:H$_2$O), 20 °C, CAN (1 g, 1.82 mmol) as sacrificial oxidant, 1000 rpm stirring speed) was measured for Ru(bda) dialdehyde 1 as molecular model compound and the 2nd order rate constant $k_1 = 1.48 \times 10^5$ L mol$^{-1}$ s$^{-1}$ was obtained by a linear fit of the initial rate of O$_2$ evolution versus the square of catalyst concentration (Figure S52b). For comparison, we calculated the molar concentration of Ru in Ru(bda)-COF suspensions for chemical water oxidation (711.689 g mol$^{-1}$ for C$_{36.5}$H$_{24}$N$_6$O$_4$Ru) and plotted the initial rate of O$_2$ evolution (see Table S5) against the square of this concentration to obtain a 2nd order rate constant $k_{Ru(bda)-COF} = 8.50 \times 10^2$ L mol$^{-1}$ s$^{-1}$. To take into account that for an I2M mechanism with a bimolecular O–O bond formation between two COF particles, only Ru centers at the surface of the nanoparticles are catalytically active, we estimated the ratio between surface and bulk Ru for spherical nanoparticles of different size. Based on SEM (Figure S23), Ru(bda)-COF nanoparticles utilized for chemical water oxidation are primarily in this size regime. To estimate the activity of the catalytically active surface sites, we adjusted the effective concentration of Ru at the nanoparticle interfaces and plotted the initial rate of O$_2$ evolution against the square of the concentration to obtain 2nd order rate constants $k_{surface}$ in the range of 0.94–3.78 $\times$ 10$^6$ L mol$^{-1}$ s$^{-1}$. The approximately tenfold increase of the rate constant in comparison to the molecular model compound 1 clearly indicates the proposed cooperative effect of the ordered alignment of well-defined Ru catalysts in crystalline Ru(bda)-COF, as the molecular activity of Ru(bda) is significantly enhanced after immobilization in the heterogeneous framework. In reality, this effect might even be higher as the actual amount of accessible Ru catalysts at the interface will be lower due to grain boundaries (crystallite size of ~15 nm, see Figs. S32, S33) and other defects.

Figure S52. Plot of initial catalysis rate versus a) concentration and b) square of concentration for Ru(bda) dialdehyde 1 (black), Ru(bda)-COF (red) and Ru(bda)-COF with adjusted concentration of active Ru centers at the surface of nanoparticles with 200 and 400 nm.
Figure S53. Time-dependent O$_2$ evolution for various amounts of Ru(bda)-monomer (a) and Ru(bda)-aldehyde (d) (3.4 mL of aqueous solution using CAN (0.54 M) as a sacrificial oxidant, 20 °C, pH = 1 (CF$_3$SO$_2$H:H$_2$O), 1000 rpm stirring speed). b) and e) Plots of initial catalysis rates (obtained by linear fit of O$_2$ evolution curve for the first 5 seconds of catalysis) versus WOC concentration with corresponding quadratic regression fit for monomer and aldehyde respectively. c) and f) Plots of initial catalyst rate versus square of catalyst concentration with linear regression fit for monomer and aldehyde respectively.
Section S7. Spectroscopy

**X-ray photoelectron spectroscopy**

According to the universal curve, the electron mean-free path, i.e., the probing depth of this experiment was on the order of 0.5 to 2 nm for the investigated core levels. From the spectrum of O1s, it could be observed the enhancement of oxygen content after the catalysis. This might come from the coordinated water with the Ru centre after the catalysis.

![Figure S54](image1)

**Figure S54.** XPS spectra of Ru(bda)-COF for regions N 1s (b) Ru 3p (c) and O 1s (d).

**UV–vis spectroscopy**

![Figure S55](image2)

**Figure S55.** UV–vis diffuse reflectance (DR) spectrum of the Ru(bda)-COF before (red) and after (green) the catalysis measured in the solid state referenced to barium sulphate.
Section S8. References

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