Supporting Information

Understanding entrapped molecular photosystem and metal-organic framework synergy for improved solar fuel production

Philip M. Stanley,[a,b] Mykhaylo Parkulab,[a] Bernhard Rieger,[b] Julien Warnan,[a,*] and Roland A. Fischer[a,*]

a Chair of Inorganic and Metal-Organic Chemistry, Department of Chemistry and Catalysis Research Center, Technical University of Munich, Lichtenbergstraße 4, Garching, 85787, Germany.

b WACKER-Chair of Macromolecular Chemistry, Department of Chemistry and Catalysis Research Center, Technical University of Munich, Lichtenbergstraße 4, Garching, 85787, Germany.

Table of Contents

1. Analytical methods, calculations, and characterization techniques

Adsorption measurements

Adsorption measurements with N_2 (99.999 vol%) at 77 K and CO_2 (99.995 vol%) at 298 K were carried out on a 3Flex Physisorption from *Micromeritics Instrument Corp.*, which uses a volumetric method to determine the amount adsorbed under an equilibrated gas pressure. Adsorption data was processed using the 3Flex Software Version 5.01 by *Micromeritics Instrument Corp.* and plotted in OriginPro 2019b by *OriginLab Corp.* Samples were transferred into pre-weighed sample tubes and capped with *Micromeritics* CheckSeals. Samples were subsequently activated at 393 K for 16 hours under dynamic vacuum of approx. 10^{-3} mbar using a SmartVac Prep by *Micromeritics Instrument Corp.* to ensure absence of unwanted adsorbates and identical pre-measurement states of all samples. The mass of the adsorbents was then recorded, generally in the range of 25 - 100 mg. Free space of the sample tube was determined prior to measuring each adsorption isotherm using Helium (99.999 vol%). A liquid nitrogen bath was used for measurements at 77 K.

The apparent surface area was derived using the Brunauer-Emmett-Teller (BET) model, is hence given as the 'BET area' and based on N_2 isotherms measured at 77 K. To determine this value for microporous materials, care was taken to adhere to the Rouquerol criteria.[1,2]

The pore size distribution (PSD) was derived by fitting N_2 isotherms measured at 77 K with sets of theoretical isotherms (kernel) derived from two-dimensional non-local-density functional theory (2D-NLDFT) based methods for specific pore sizes and geometry. As an approximation, cylindrical pores on an oxide surface were assumed for all materials to allow comparability within this series. Fitting was done using the respective kernel available via the 3Flex Software Version 5.01 by *Micromeritics Instrument Corp.*

Density functional theory (DFT) optimisations and modelling

The applied sacrificial electron donors and additive bases were optimised on a B3LYP/6-311G* level using GaussView 6.0 and Gaussian 16W. Atomic coordinates of the optimised structures are available in chapter S6.

Infrared spectroscopy (ATR-IR)

A *PerkinElmer* Frontier FT-IR spectrometer featuring an ATR plate with a germanium crystal was used with a 2 cm^{-1} resolution and 16 accumulated scans.

Nuclear magnetic resonance (NMR)

Liquid state NMR spectra were recorded by a *Bruker* Ultrashield DRX400 (^{1}H: 400.13 MHz) at ambient temperature (298 K). The ^{1}H NMR spectroscopic chemical shifts δ are reported in ppm relative to tetramethylsilane. ^{1}H NMR spectra are calibrated against the residual proton and natural abundance carbon resonances of the respective deuterated solvent as an internal standard (CD_3CN: δ (^{1}H) = 2.15 ppm, DMSO-d_6: δ (^{1}H) = 2.50 ppm). The following abbreviations are used to describe signal multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet.

Gas chromatography (GC)

Photocatalytic reaction analysis was conducted via measuring the gas composition of the reaction headspace. This was done with a *SRI Instruments Europe* Model 8610C, with a methanizer, FID and TCD detector, a MoleSieve 13X and silica gel column with N_2 as the carrier gas. After sample injection onto the column at 50 °C, a temperature program of a 1.2 min hold at 50 °C, heating to 110 °C with 10 °C/min, 2.0 min hold at 110 °C, cooling to 50 °C with 50 °C/min and a 5 min hold at 50 °C is applied with subsequent analysis over both columns. These parameters provide complete and quantitative separation of potential hydrogen, nitrogen/air, CO, methane, and CO_2 in the sample. CO was calibrated with several reference ppm gases from *Air Products GmbH* for accurate quantification.

Molecular loading within the MOF

MIL-101-NH_2(Al) consists of two different mesoporous cage types, one large cage accessible through a hexagonal 16 Å window, and a small cage accessible through a pentagonal 12 Å window. The large and small cages occur in a ratio of 1 to 2 and are constructed from 84 and 60 linkers, respectively. Each linker is in turn shared by two cages, giving a weighted average of 34 linkers per cage. Using the molecular formula $Al_3O(Cl)(H_2O)_2(C_8H_3O_4NH_2)_3$ with a molecular weight of 705.82 g/mol for MIL-101-NH_2(Al),[3] each 2-aminoterephthalic acid linker is assigned a mean molecular weight of 235.27 g/mol. Thus, the mean molecular weight per cage is 7999.3 g/mol. This value in turn provides a molar cage concentration n_{cages} = 125.01 nmol/mg_{MOF}, with n_{cages_small} = 83.34 nmol/mg_{MOF} and n_{cages_large} = 41.67 nmol/mg_{MOF}.[4]

The molecular complexes $ReBr(CO)_3$(4,4'-dcbpy) and $Ru(bpy)_2$(5,5'-dcbpy)Cl_2 possess molecular diameters of 12.5 Å and 14.5 Å.[5] They are sterically blocked from entering the small cages through the smaller pentagonal window and are immobilized in the large cages.[4–6] Consequentially, the average number of immobilized molecules per large cage is calculated as follows, using experimental ICP-MS data (Table S1):

$$\frac{\text{Maximum attained experimental molar loading}}{\text{Molar large cage concentration}} = \frac{n_{exp\_max}}{n_{cages\_large}} = \frac{109\ \text{nmol/mg}_{MOF}}{41.7\ \text{nmol/mg}_{MOF}} = 2.6$$

This implies a distribution of two and three complexes per cage. Correspondingly, with increasing Ru/Re molar immobilization ratios it becomes less and less probable that two catalysts are present in the same cage.

The attained maximum loading of 109 ± 3 nmol/mg_{MOF} corresponds to the following mol%:

$$\frac{n_{exp\_max}}{n_{MIL\text{-}101\text{-}NH2(Al)}} = \frac{n_{exp\_max} \cdot M_{MIL\text{-}101\text{-}NH2(Al)}}{m_{MIL\text{-}101\text{-}NH2(Al)}} = \frac{109\ \text{nmol} \cdot 705.82\ \text{ng/nmol}}{1 \cdot 10^6\ \text{ng}} = 7.7\ \text{mol\%}$$

Photocatalytic CO_2 reduction

Photocatalytic tests were performed in air-tight 25 mL reaction vials with the respective MOF material (0.5 mg), acetonitrile (4 mL), a stir bar, and a sacrificial electron donor (1.5 mmol). The reaction suspension and headspace were fully saturated with CO_2 for seven minutes and after sealing the vial a CO_2 overpressure was applied, totalling a pressure of 1.45 bar. The

irradiation source was eight individual LEDs (Blue LED LXZ1 PR01) at λ = 450 nm and a constant photon flux was set by a power supply (5.1 W). GC analysis of the reaction headspace was conducted at time intervals by taking a gas aliquot through the reaction cap sept.

For further cycles with replenished photosensitizer, the solid was separated from the used reaction mixture by filtration and washed twice with fresh acetonitrile. It was then immersed in a 0.05 mM $Ru(bpy)_2(5,5'\text{-}dcbpy)Cl_2$ solution (20 mL) in acetonitrile for 3 hours, washed twice with fresh acetonitrile, and dried at 80 °C. Subsequently, the standard photocatalytic test procedure was repeated. For the homogeneous counterpart studies, 0.5 µmol $Ru(bpy)_2(dcbpy)Cl_2$ and 0.2 mL fresh TEOA are added to the reaction mixture, before conducting the standard photocatalytic test procedure.

Photocatalysis Turnover Number (TON) and MOF/Homog. Calculations

For every photocatalytic carbon dioxide reduction experiment the TONs were calculated as follows. The exact molar catalyst amount was obtained through multiplying the $\mu mol/mg_{MOF}$ values from ICP-MS analysis with the weigh-in, typically 3.5 mg. Subsequently, the Micro-GC headspace analysis provided area% results for each gas present. For carbon monoxide, these were then converted to vol%, volume, and moles in turn. To account for solvated CO in MeCN, Henry's law was used and the formulas, values and an exemplary TON calculation is provided after Table S2.[7,8]

Calculation of MOF/Homog. used to compare MOF samples to homogeneous conditions:

$$MOF/Homog. = \frac{\mathrm{TON}_{\mathrm{SED,MOF}}}{\mathrm{TON}_{\mathrm{SED,Homog.}}}$$

Exemplary calculation for SED = BIH (TON data in Table S4):

$$MOF/Homog. = \frac{\mathrm{TON}_{\mathrm{BIH,MOF}}}{\mathrm{TON}_{\mathrm{BIH,Homog.}}} = \frac{344}{182} = 1.9$$

Powder x-ray diffraction (PXRD)

PXRD measurements were performed on a silicon single-crystal wafer using *Bragg-Brentano* geometry in a *Rigaku* MiniFlex 600-C diffractometer. X-ray Cu K_α radiation (λ_1 - 1.5406 Å, λ_2 - 1.5444 Å, I_2/I_1 - 0.5) was used and K_β radiation was removed by a Ni-filter. The measurement range, unless stated otherwise, was from 5.0° to 50.0° (2θ) with a step size of 0.010 degrees and a scan rate of 5 degrees per minute.

Scanning electron microscopy (SEM)

SEM images were obtained with a *Jeol* JSM-7500F field emission scanning electron microscope with the Gentle Beam mode.

Scherrer equation for calculating the mean ordered crystalline domain size

The *Scherrer* equation, as depicted below, was used to calculate the mean ordered crystalline domain size τ (nm) of the MOFs.[9] With *K* as the shape factor, λ as the x-ray wavelength (nm), β as the line broadening at half the maximum intensity (FWHM) and ϑ as the Bragg angle.

$$\tau = \frac{K\lambda}{\beta\cos(\theta)}$$

Example calculation: K = 0.94 (spherical objects); λ = 0.154 nm; 2θ = 3.35° (311 reflex, θ = 1.675°; in radian: 0.0292) and FWHM: 0.21 (in radian: 0.0037)

$$\tau_{(311)} = \frac{0.94 \cdot 0.154\ \text{nm}}{0.0037 \cdot \cos(0.0292)} = 39.6\ \text{nm}$$

Applying this formula to the intense (311), (511), and (911) reflexes yields $\tau = 36.3\ \pm 5.7\ \text{nm}$ for all MIL samples, irrespective of the synthesis route.

Solid-state UV-Vis spectroscopy

Solid-state UV-Vis spectra were recorded on a *Shimadzu* UV-3600 Plus UV-Vis-NIR spectrophotometer. Powder samples were fixed between two quartz glass slides for measurement and baseline corrected.

Thermogravimetric analysis (TGA)

A TGA/STA 409 PC apparatus from *Mettler-Toledo Intl. Inc.* was used for thermogravimetric analysis under synthetic air with a continuous heating ramp of 10 °C/min. The corresponding evaluation software was *STARe 14.00.* Roughly 2 mg of sample were applied in aluminum oxide crucibles.

UV-Vis spectroscopy

UV-Vis spectra were recorded on an *Agilent Technologies* Cary 60 with a scan rate of 600 nm/min. Baseline correction was performed with the respective pure solvent. Each sample was measured in a QS Suprasil 10.00 mm quartz glass cuvette from *Heraeus Quarzglas GmbH.*

2. Synthetical procedures

fac-ReBr(CO)$_3$(4,4'-dcbpy) (1)

The synthesis was adapted from a literature known procedure.[10] $ReBr(CO)_5$ (0.30 g, 0.74 mmol, 1.0 eq.) was given to ethylene glycol dimethyl ether (20 mL) under inert gas conditions. To the resulting solution, 4,4'-dicarboxyl-2,2'-bipyridine (0.18 g, 0.74 mmol, 1.0 eq.) was added and the reaction mixture was stirred overnight under inert gas atmosphere at 90 °C. After cooling, the solvent was removed *in vacuo* and the resulting solid was dissolved in minimal amounts of dimethyl ether and given to hexane (100 mL) at 0 °C. The precipitate was isolated *via* centrifugation and dried *in vacuo* to give the orange product of which characterizations matched literature reports.[10]

^{1}H NMR (400 MHz, 300 K, CD_3CN): δ (ppm) = 9.20 (d, ^3J = 5.7 Hz, 2H), 8.95 (s, 2H), 8.06 (d, ^3J = 5.7 Hz, 2H); ATR-IR (σ, cm^{-1}): 1870, 1915 and 2021.

Ru(bpy)$_2$(5,5'-dcbpy)Cl$_2$ · 6 H$_2$O (2)

The synthesis was adapted from a literature known procedure.[11] $Ru(bpy)_2Cl_2$ (100.0 mg, 207 µmol, 1.00 eq.) and 5,5'-dicarboxyl-2,2'-bipyridine (64.0 mg, 262 µmol, 1.27 eq.) were given to ethanol/water (15 mL, 1/1 v/v) and refluxed for 25 hours under an inert atmosphere. After cooling, the solvent was removed *in vacuo* and the crude was recrystallized from methanol/diethyl ether (1/1 v/v). To remove trace impurities, the powder was dissolved in water, filtered, and the filtrate was evaporated to yield the dark-red crystalline product (119.4 mg, 143 µmol, 70% yield) of which characterizations matched literature reports.[11]

^{1}H NMR (400 MHz, 300 K, DMSO-d_6): δ (ppm) = 8.87 (m, 4H), 8.80 (d, ^3J = 8.3 Hz, 2H), 8.37 (d, ^3J = 8.1 Hz, 2H), 8.19 (m, 4H), 8.00 (s, 2H), 7.79 (d, ^3J = 5.6 Hz, 2H), 7.77 (d, ^3J = 5.6 Hz, 2H), 7.58 (t, ^3J = 6.5 Hz, 2H), 7.53 (t, ^3J = 6.5 Hz, 2H)

MIL-101-NH$_2$(Al) – Solvothermal approach (1.32 ± 0.34 µm sized particles)

The synthesis was adapted from a literature known procedure.[12] 2-Amino-terephthalic acid (0.680 g, 3.75 mmol, 1.00 eq.) was dissolved in DMF (100 mL) and heated to 110 °C. Subsequently, a solution of aluminium trichloride (1.00 g, 7.51 mmol, 2.00 eq.) in DMF (50 mL) was added slowly over 90 minutes. The resulting suspension was stirred for 3 hours at 110 °C and kept at 110 °C without stirring for 15 h. After cooling, the yellow precipitate was removed by centrifugation (7830 rpm, 10 minutes) and washed with DMF (3 × 50 mL) and methanol (3 × 50 mL. Further purification occurred *via* Soxhlet extraction with acetonitrile, followed by drying at 80 °C for 24 hours to yield the light-yellow MOF (765 mg).

MIL-101-NH$_2$(Al) – Microwave approach (779 ± 175 nm sized particles)

2-Amino-terephthalic acid (0.56 g, 3.1 mmol, 1.3 eq.) and anhydrous aluminium trichloride (0.31 g, 2.3 mmol, 1.0 eq.) were mixed in DMF (40 mL) and filled into a Teflon lined autoclave with a magnetic stir bar. The autoclave was loaded into a *CEM* MARS-6 microwave and heated to 130 °C with 1800 W and held at 130 °C for 2 minutes. After cooling, the yellow precipitate was washed and purified in analogous fashion to the solvothermal approach.

MIL-101-NH_2(Al) – Microwave approach (559 ± 152 nm sized particles)

The synthesis was adapted from a literature known procedure.[13] 2-Amino-terephthalic acid (0.56 g, 3.1 mmol, 1.3 eq.) and anhydrous aluminium trichloride (0.31 g, 2.3 mmol, 1.0 eq.) were mixed in DMF (40 mL) and filled into a glass autoclave with a magnetic stir bar. The autoclave was loaded into a *CEM* Discover System 908010 microwave and heated to 130 °C with 120 W and held at 130 °C for 20 minutes. After cooling, the yellow precipitate was washed and purified in analogous fashion to the solvothermal approach.

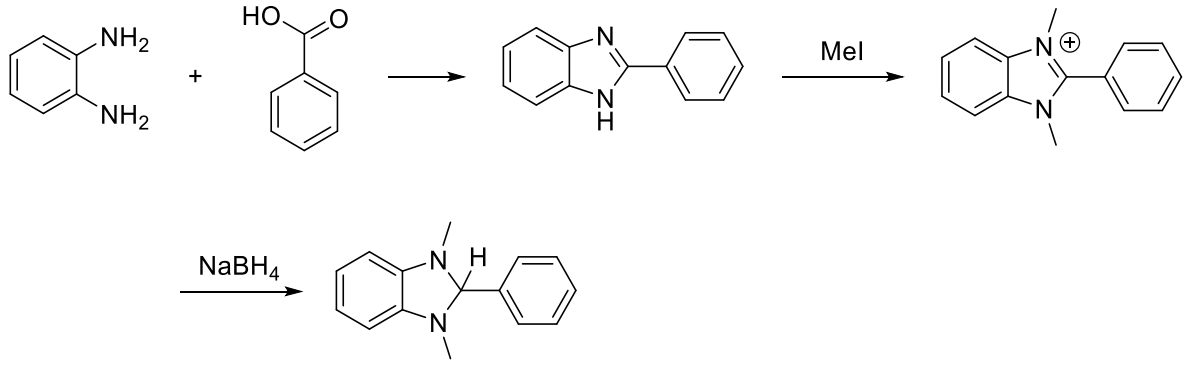
MIL-101-NH_2(Al) – Microwave and modulator approach (70 ± 18 nm sized particles)

2-Amino-terephthalic acid (1.12 g, 6.2 mmol, 2.6 eq.), anhydrous aluminium trichloride (0.31 g, 2.3 mmol, 1.0 eq.), and *p*-tert-butyl benzoic acid (0.41 g, 3.0 eq.) as a modulator were mixed in DMF (40 mL) and filled into a glass autoclave with a magnetic stir bar. The autoclave was loaded into a *CEM* Discover System 908010 microwave and heated to 130 °C with 120 W and held at 130 °C for 20 minutes. After cooling, the yellow precipitate was washed and purified in analogous fashion to the solvothermal approach.

Molecular complex entrapment: ReRu-MIL

Typically, as synthesized MIL-101-NH_2(Al) (50.0 mg) was immersed in a solution of **1** (0.59 mg, 1 µmol) and **2** (8.3 mg, 10 µmol) in MeCN (140 mL) for 24 h. Then the supernatant was removed by filtration, and the resulting orange powder was washed with fresh acetonitrile for four hours respectively (3 × 10 mL). Finally, the powder was dried overnight at 80 °C.

1,3-Dimethyl-2-phenyl-2,3-dihydro-*1H*-benzo[*d*]imidazole (BIH)



Polyphosphoric acid (10.5 g), benzoic acid (3.07 g, 25.1 mmol, 1.0 eq.) and *o*-phenylenediamine (2.71 g, 25.1 mmol, 1.0 eq.) were stirred at 180 °C for 2 h. Subsequently, ammonia solution (50 mL, 6% in H_2O) was added and the purple product was isolated and washed with ammonia solution and dried *in vacuo* to yield 2-phenyl-1H-benzo[d]imidazole (4.83 g, 24.8 mmol, 99% yield).

NaOH (1.04 g, 25.8 mmol, 1.04 eq.) and methanol (25 mL) were added to 2-phenyl-1H-benzo[d]imidazole (4.83 g, 24.8 mmol, 1.0 eq.). Methyl iodide (5.64 mL, 90.8 mmol, 3.65 eq.) was added to the suspension and reflexed for 48 h. The solvent was removed *in vacuo*, the crude product was dissolved in hot ethanol/H_2O (5/1 v/v, 160 mL) and activated carbon was added. After 30 min, the slurry was filtered hot over a celite pad, the solvent was removed *in*

vacuo and the resulting solid was recrystallized from ethanol to yield 1,3-dimethyl-2-phenyl-1H-benzo[d]imidazole-3-ium iodide (5.44 g, 15.5 mmol, 62% yield) as light yellow needles.

^{1}H NMR (400 MHz, 300 K, DMSO-d_6) δ (ppm) = 8.13 (m, 2H), 7.76 (m, 2H), 7.92 (m, 5H), 3.92 (s, 6H)

1,3-dimethyl-2-phenyl-1H-benzo[d]imidazole-3-ium iodide (5.44 g, 15.5 mmol, 1.0 eq.) was dissolved in dry methanol (150 mL) and sodium borohydride (2.16 g, 57.0 mmol, 3.7 eq.) was added under inert conditions. After 1 h of stirring at room temperature, the solvent was removed *in vacuo* and the crude product recrystallized from ethanol/H_2O (2/1 v/v) to yield 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (3.1 g, 13.8 mmol, 89%) as white needles.

^{1}H NMR (400 MHz, 300 K, DMSO-d_6): δ (ppm) = 7.55 (m, 2H), 7.44 (m, 3H), 6.61 (m, 2H), 6.45 (m, 2H), 4.87 (s, 1H), 2.48 (s, 6H)

Elemental analysis: Calculated for $C_{15}H_{16}N_2$: C 80.32; H 7.19; N 12.49. Found: C 79.93; H 7.20; N 12.41.

3. Supporting Figures

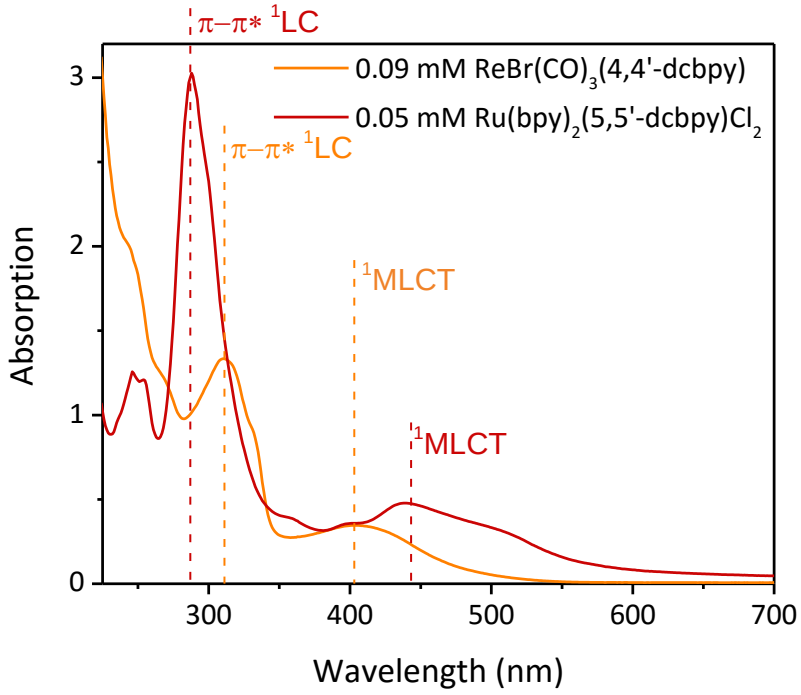


Figure S1: UV-Vis spectra of a 0.09 mM of **1** $ReBr(CO)_3$(4,4'-dcbpy) (orange) and a 0.05 mM solution of **2** $Ru(bpy)_2$(5,5'-dcbpy)Cl_2 (red) in acetonitrile.

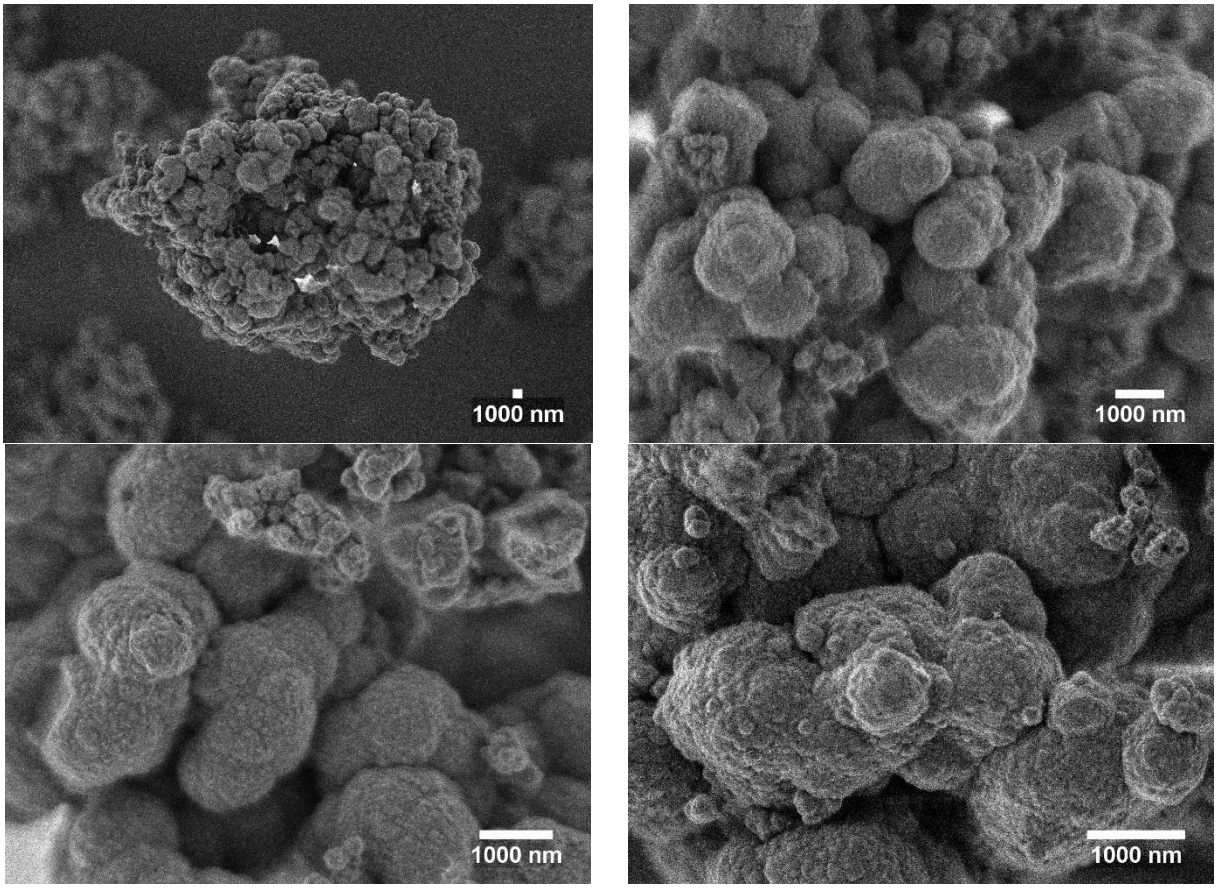


Figure S2: SEM images of MIL-101-NH_2(Al) synthesised via the solvothermal method.

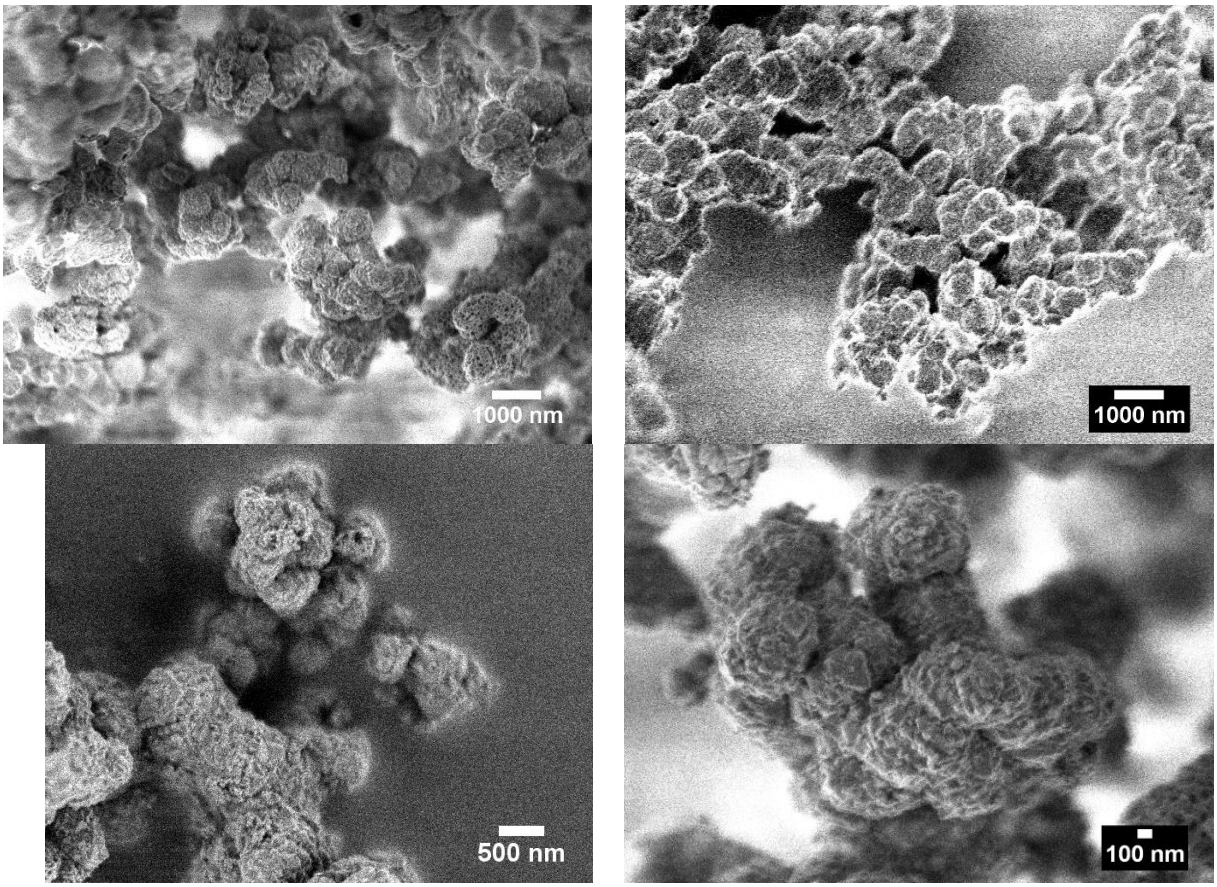


Figure S3: SEM images of MIL-101-NH_2(Al) with the microwave approach (1800 W).

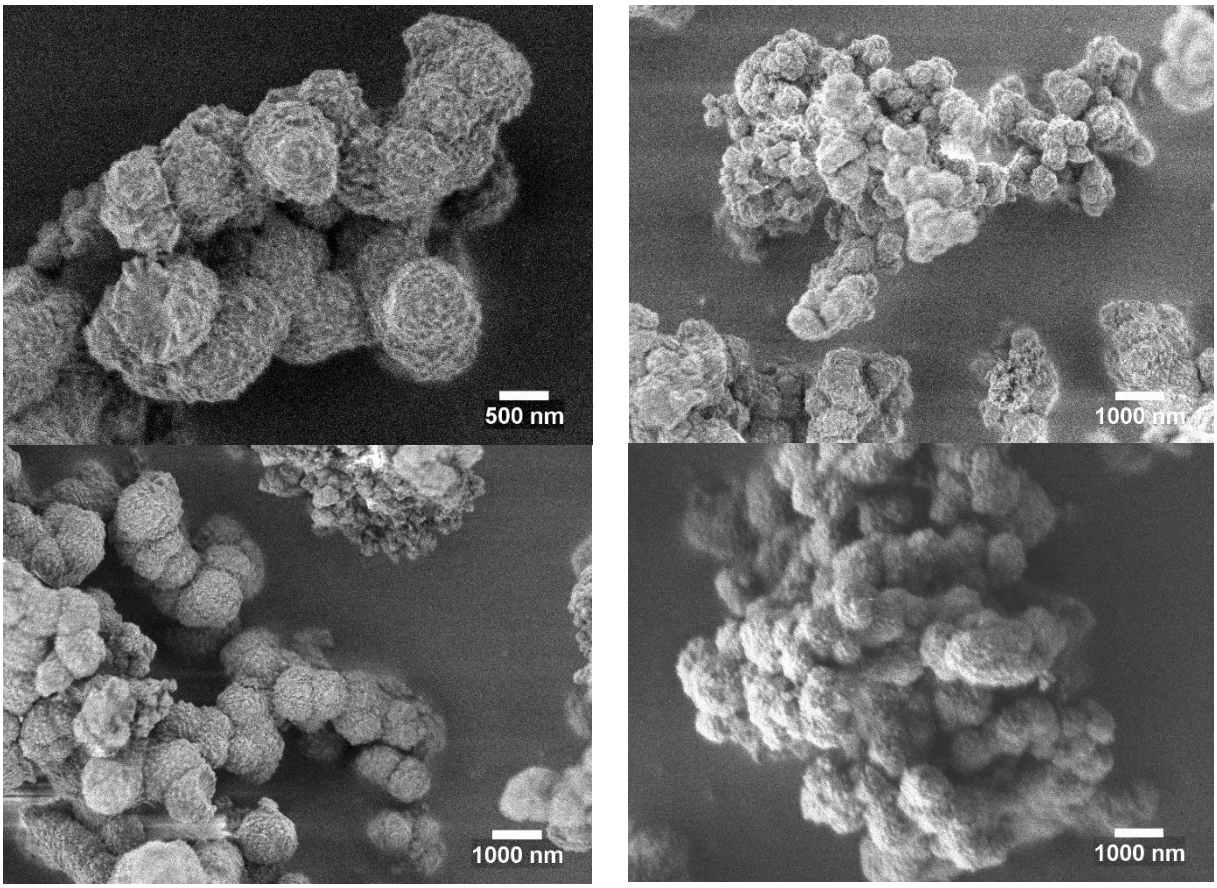


Figure S4: SEM images of MIL-101-NH_2(Al) with the microwave approach (120 W).

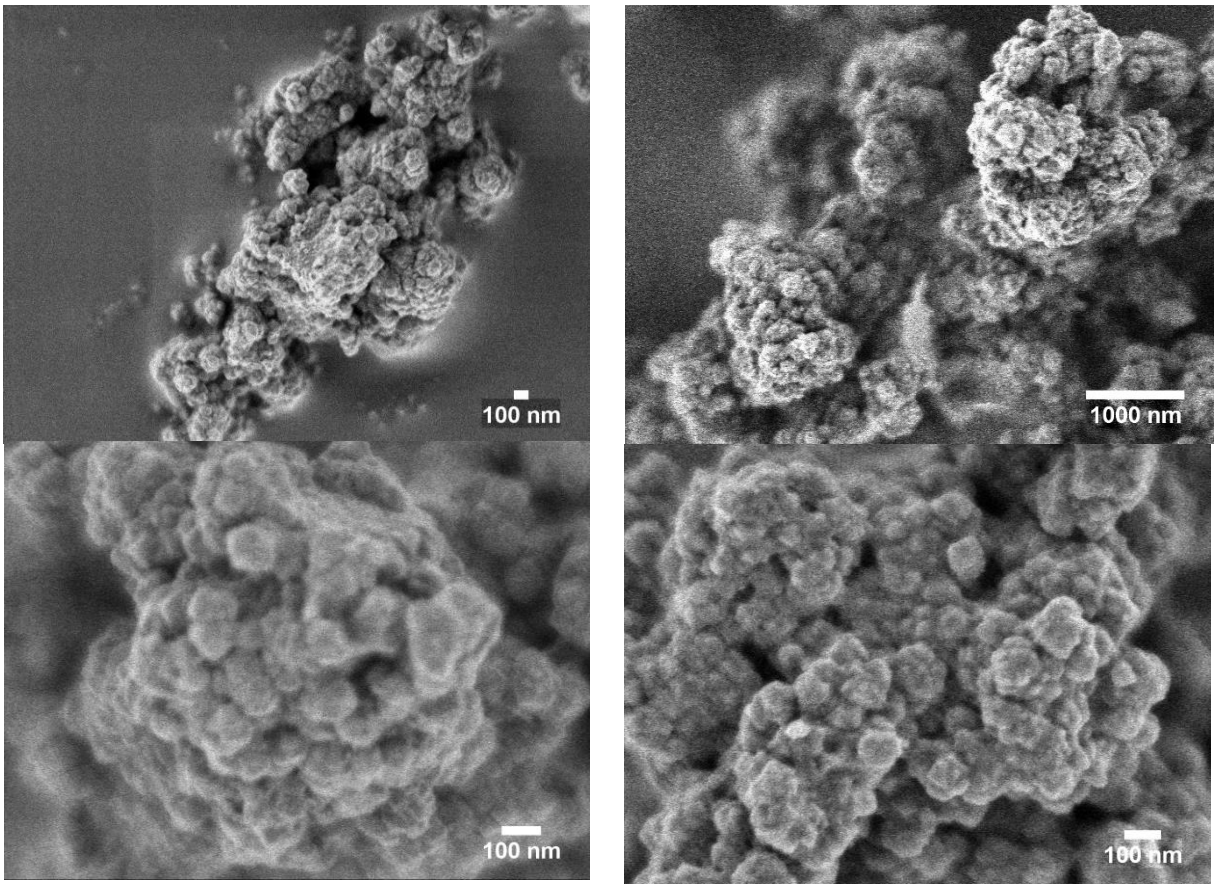


Figure S5: SEM images of MIL-101-NH_2(Al) with the microwave approach (120 W) with *p-tert*-butyl benzoic acid as a modulator.

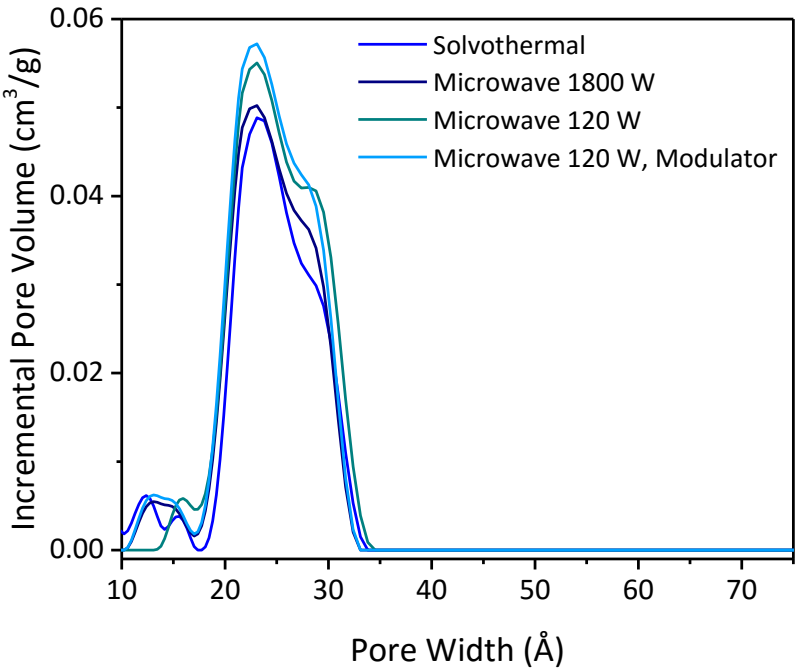


Figure S6: Calculated pore size distribution from the N_2 adsorption isotherms in Figure 3b for as synthesised MIL-101-NH_2(Al) samples with sets of theoretical isotherms (kernel) derived from two-dimensional non-local-density functional theory (2D-NLDFT) based methods for specific pore sizes and geometry. As an approximation, cylindrical pores on an oxide surface are assumed.

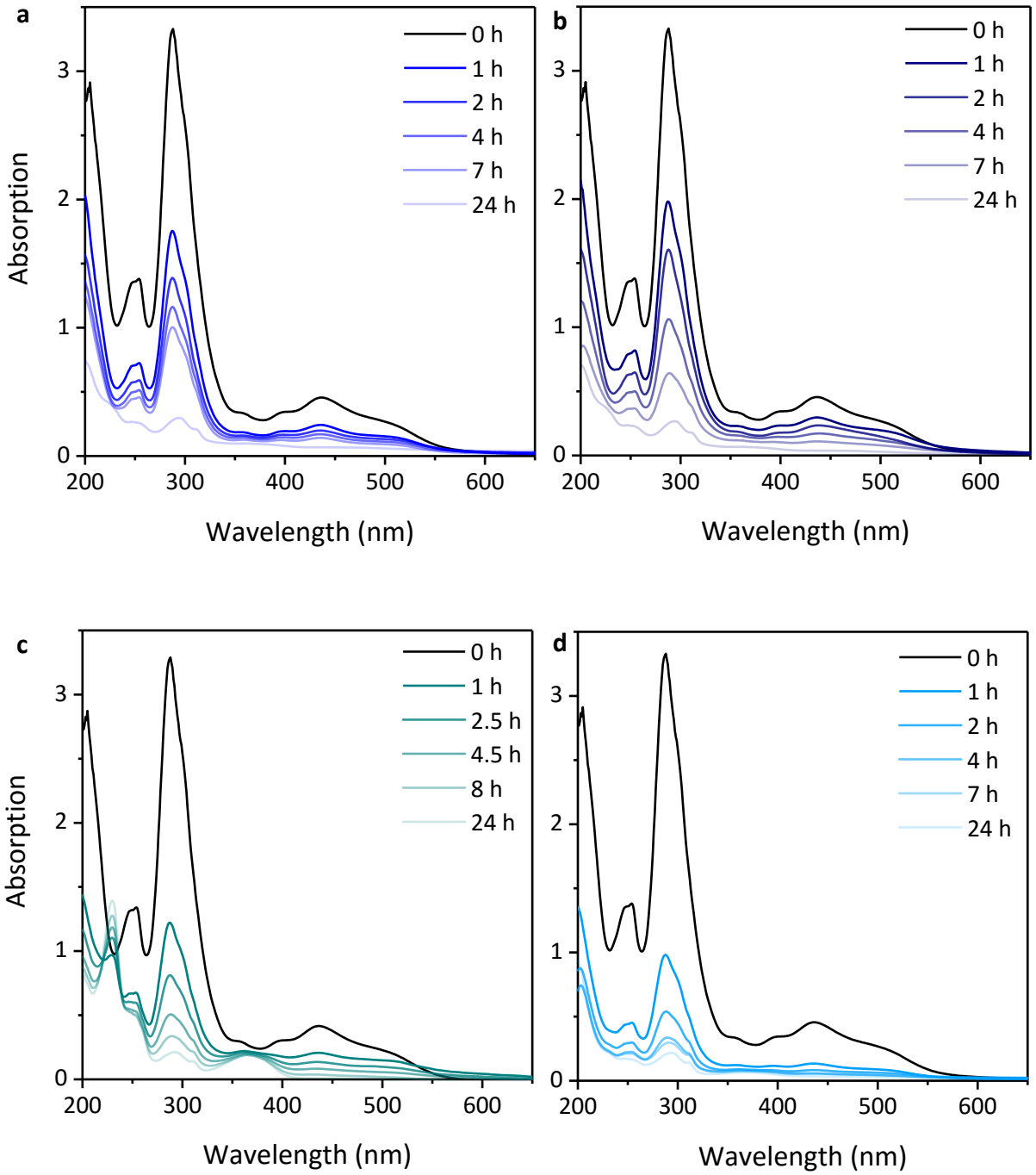


Figure S7: UV-Vis spectra of solutions of the CRC **1** (5.5 µg, 1 nmol) and the PS **2** (83 µg, 10 nmol) in MeCN (10 mL) for 24 hours in presence of 5.0 mg of MIL-101-NH_2(Al) obtained from: **a** solvothermal synthesis (1320 nm). **b** microwave assisted MOF synthesis at 1800 W (779 nm). **c** microwave assisted MOF synthesis at 120 W (559 nm). **d** microwave assisted MOF synthesis at 120 W with 3 eq. of *p-tert*-butyl benzoic acid as a modulator (70 nm).

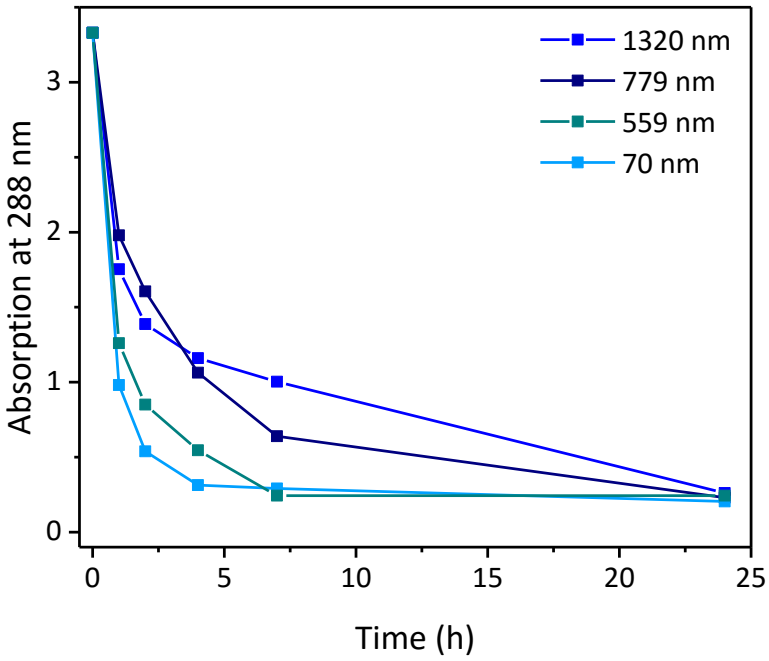


Figure S8: Absorption band maximum monitoring during entrapment of **1** and **2** in MeCN. Taken from the full spectra shown in Figure S7.

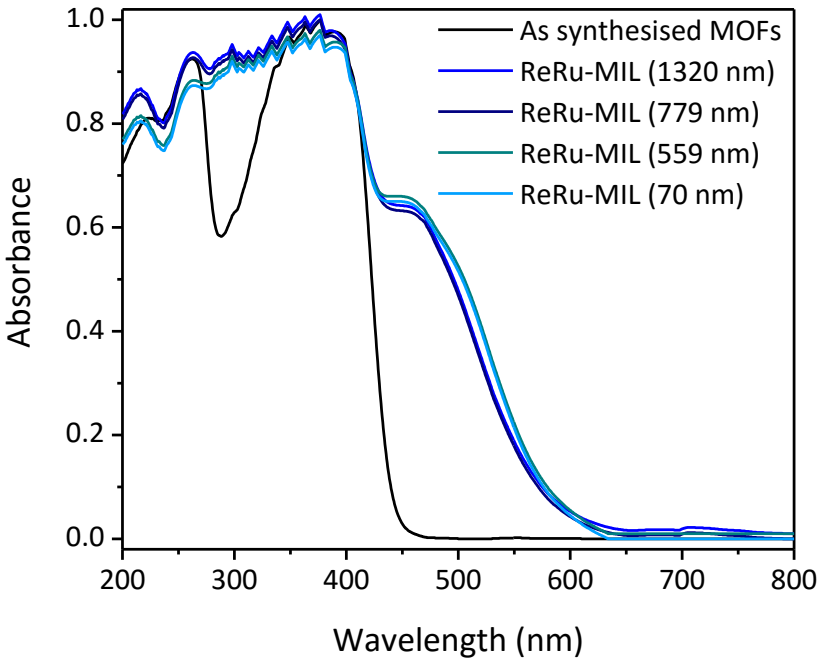


Figure S9: Normalized solid-state UV-Vis spectra of as synthesised MIL-101-NH_2(Al) samples (black) and ReRu-MIL assemblies with entrapped **1** and **2** and different particle sizes (blue shades).

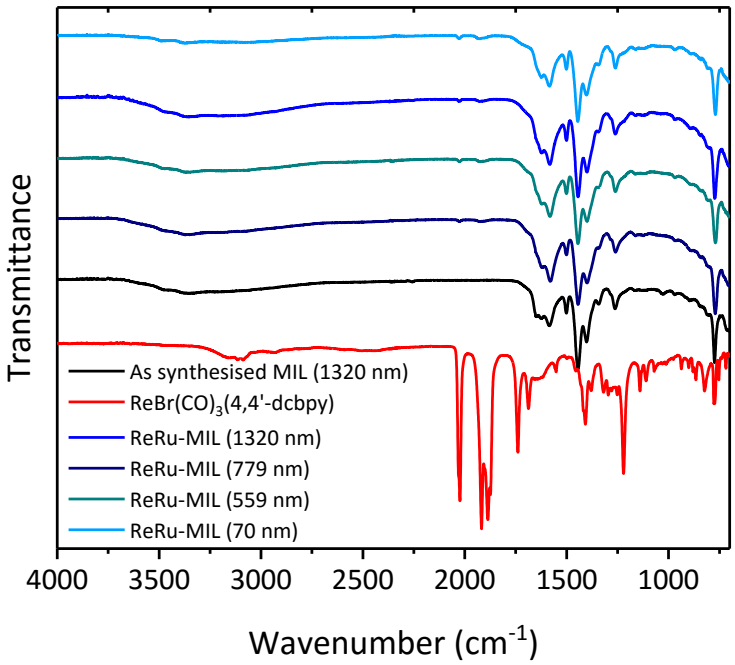


Figure S10: IR spectra of as synthesised MIL-101-NH_2(Al) (1320 nm, black), pure $ReBr(CO)_3$(4,4'-dcbpy) **1** (red), and ReRu-MIL assemblies with entrapped **1** and **2** (blue shades).

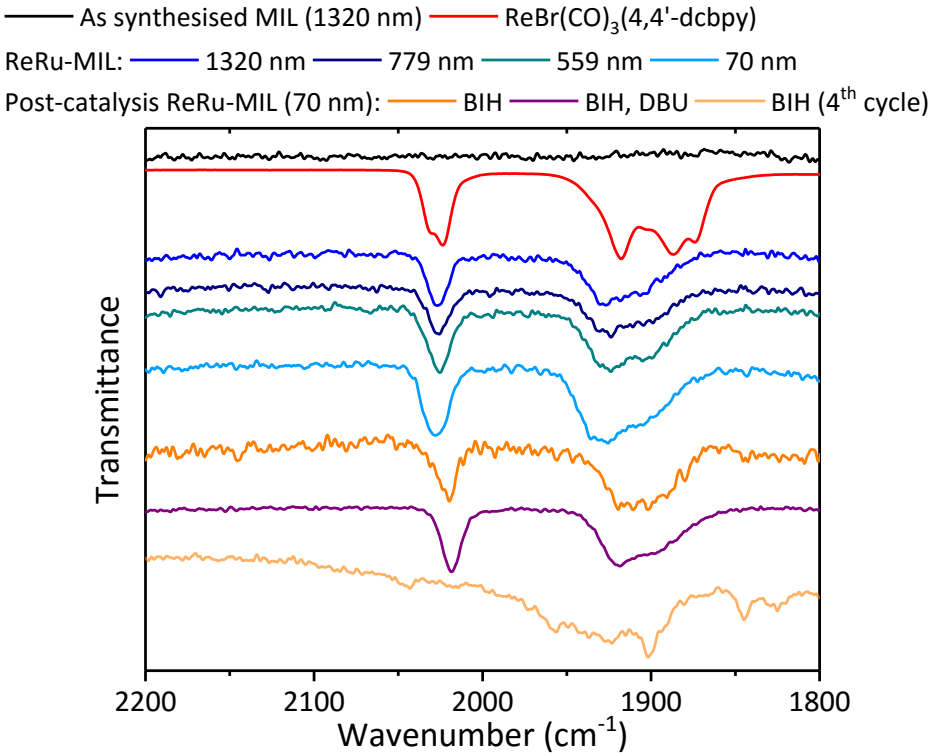


Figure S11: Detailed IR spectra between 1800 and 2200 cm^{-1} of as synthesised MIL-101-NH_2(Al) (1320 nm, black), pure molecular complex $ReBr(CO)_3$(4,4'-dcbpy) **1** (red), ReRu-MIL assemblies with entrapped **1** and **2** and different particle sizes (blue shades), and post-catalysis (24 h irradiation at 450 nm under standard reaction conditions) of ReRu-MIL (70 nm) (orange, purple) and after 96 h irradiation (yellow).

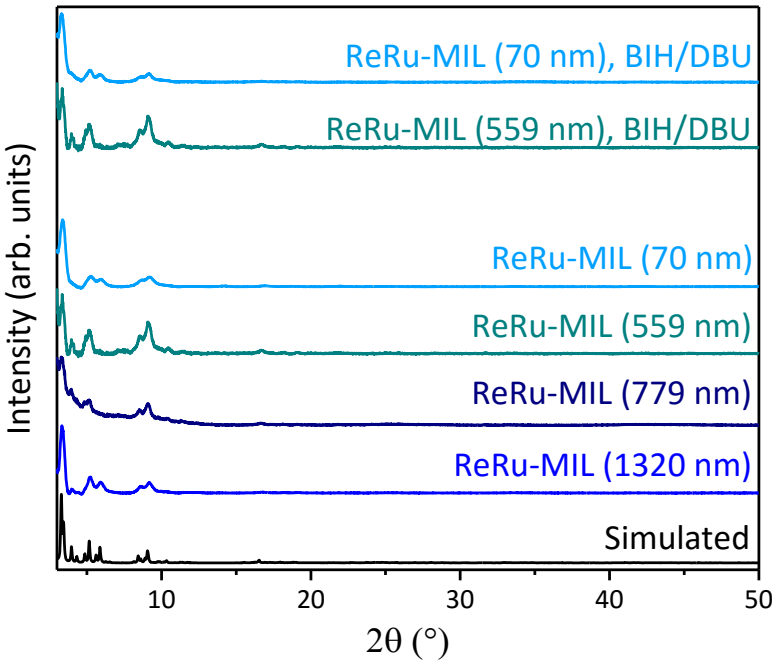


Figure S12: PXRD diffractograms of ReRu-MIL MOF assemblies. Lower five: Samples with different particle sizes (blue shades) after post-synthetic entrapment of **1** and **2** and calculated reflexes for MIL-101(Cr) (CCDC Number 605510). Top two: Post-catalysis ReRu-MIL samples with different particle sizes (blue shades) after 24 hours irradiation at 450 nm with BIH (1.5 mmol) and DBU (0.15 mmol).

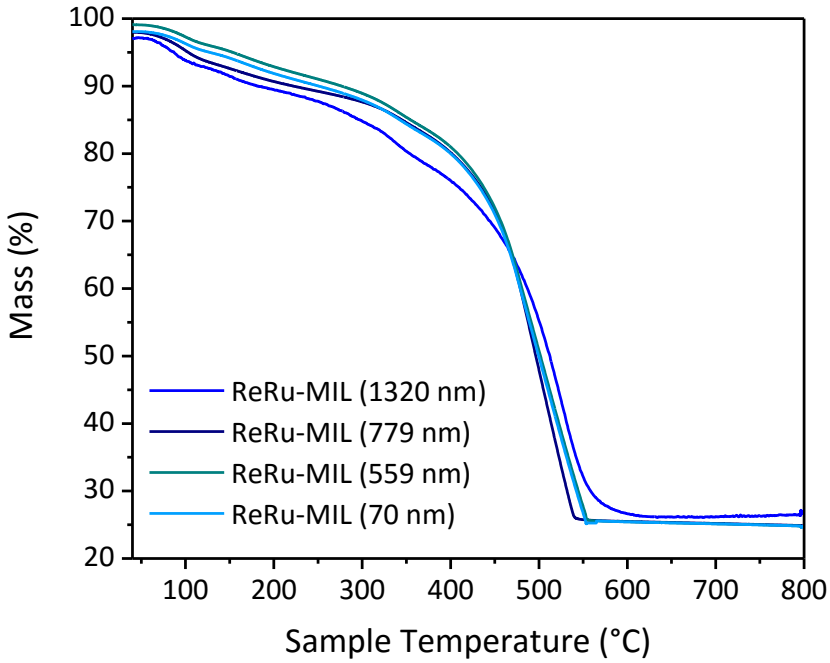


Figure S13: TGA curves of ReRu-MIL assemblies with entrapped **1** and **2** and different particle sizes (blue shades).

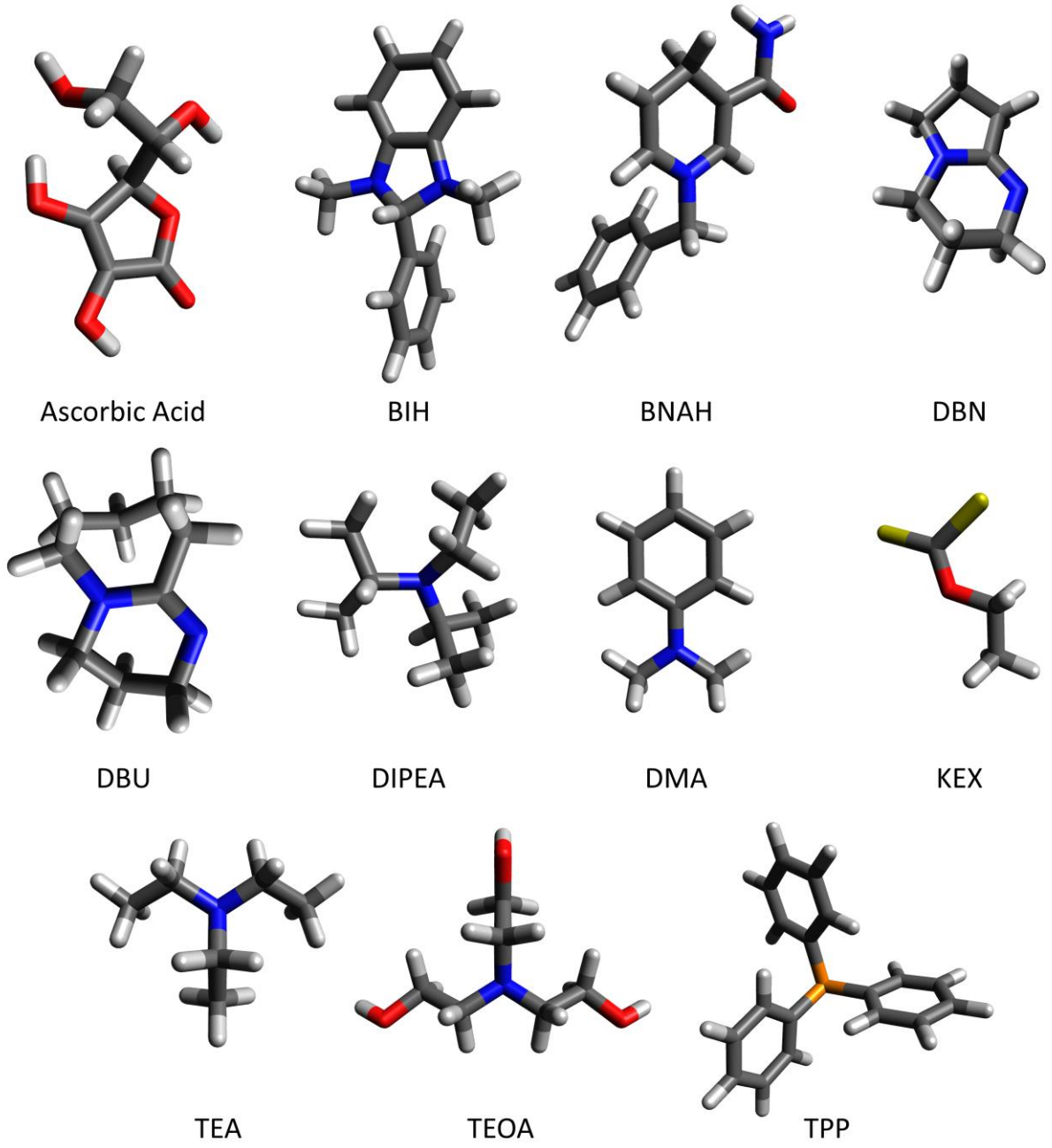


Figure S14: DFT optimised molecular structures of the applied sacrificial electron donors and additive bases at the B3LYP/6-311G*. Measured maximum molecule diameter listed in Table S3. White: H, Grey: C, Red: O, Blue: N, Orange: P, Yellow: S.

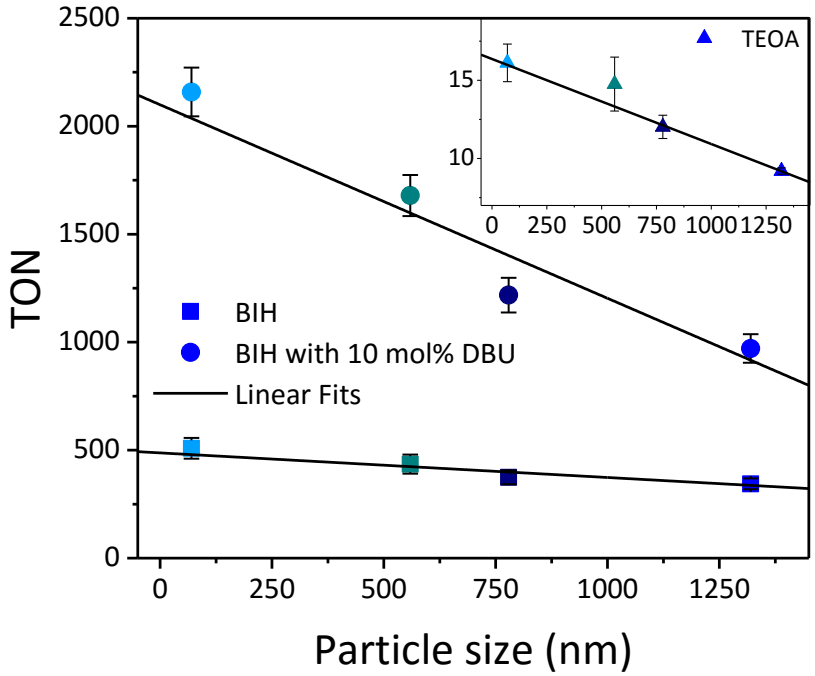


Figure S15: TON vs particle size plot for **ReRu-MIL** samples in photocatalytic CO_2-to-CO reduction. MeCN, 450 nm irradiation, 10 h. Top right inset: TEOA as the SED, see Figure 3c. Squares: BIH as the SED. Circles: BIH as the SED with 10 mol% (respective to BIH) DBU added.

4. Supporting Tables

Table S1: ICP-MS measurement values for metal Re and Ru content in various MIL-101-NH_2(Al) samples and the resulting PS/CRC ratios entrapped.

Sample	Re mass (m) [µg]	Ru mass (m) [µg]	Sample mass (m) [mg]	Re [nmol/ mg_{MOF}]	Ru [nmol/ mg_{MOF}]	PS/CRC	Loading (n) [nmol/ mg_{MOF}]
ReRu-MIL (1320 nm)	3.80 ± 0.03	16.31 ± 0.07	1.70	12.00 ± 0.09	94.92 ± 0.40	7.91	106.9 ± 0.3
ReRu-MIL (779 nm)	9.60 ± 0.06	42.53 ± 0.29	4.28	12.05 ± 0.08	98.83 ± 0.68	8.16	110.3 ± 0.4
ReRu-MIL (559 nm)	3.06 ± 0.01	13.57 ± 0.04	1.36	12.08 ± 0.04	98.72 ± 0.29	8.17	110.8 ± 0.2
ReRu-MIL (70 nm)	4.11 ± 0.06	17.60 ± 0.07	1.83	12.04 ± 0.12	95.17 ± 0.37	7.90	107.2 ± 0.2

Table S2: First cycle TON values for the photocatalytic reduction of CO_2 to CO. Standard conditions, unless specified otherwise: 0.5 mg MOF assembly, 4 mL MeCN, 0.2 mL TEOA, 10 hours, irradiation at 450 nm. Values average three repetitions under identical conditions.

Sample	Comment	TON	Activity [h]
1 (0.5 µmol)	No TEOA	n.-d.	N.A.
	No Irradiation	n.-d.	N.A.
	/	11.2 ± 0.3	0.3
1 (0.5 µmol) and **2** (4.0 µmol)	PS/CRC 8.0	11.2 ± 0.3	1.8
ReRu-MIL	D = 1320 nm	9.2 ± 0.2	10
	D = 779 nm	12.0 ± 0.7	10
	D = 559 nm	14.8 ± 1.7	10
	D = 70 nm	16.1 ± 1.2	10
ReRu-MIL (1320 nm)	No TEOA	n.-d.	N.A.
ReRu-MIL	No irradiation	n.-d.	N.A.
MIL-101-NH_2(Al)	With TEOA	n.-d.	N.A.
MIL-101-NH_2(Al)	No TEOA	n.-d.	N.A.

Calculation of Turnover Numbers (TONs)

For every photocatalytic carbon dioxide reduction experiment the TONs were calculated as follows. The exact molar catalyst amount was obtained through multiplying the µmol/mg_{MOF} values from ICP-MS analysis with the weigh-in. Subsequently, the GC headspace analysis provided ppm results for each gas present, as previously calibrated with purchased reference standards. For carbon monoxide, these were then converted to moles with the following formulas. To account for solvated CO in MeCN, Henry's law was used with a Henry constant of 2507 bar·mol_{MeCN}·mol_{CO}^{-1}.[7,8] An exemplary calculation is provided below for ReRu-MIL (70 nm) with full measurement data for a catalytic run with 4 mL MeCN, 340 mg BIH (1.5 mmol), and 22.6 µL DBU (150 µmol).

$$n_{\mathrm{Re}}[\mu\mathrm{mol}] = n_{\mathrm{Re}}\left[\frac{\mathrm{nmol}}{\mathrm{mg_{MOF}}}\right] \cdot m_{\mathrm{Sample}} = 12.0\ \frac{\mathrm{nmol}}{\mathrm{mg_{MOF}}} \cdot 0.61\ \mathrm{mg} = 7.32\ \mathrm{nmol}$$

$$Vol\%_{\mathrm{CO}} = \frac{\mathrm{ppm_{CO}}}{10000} = \frac{12212}{10000} = 1.2212$$

$$V_{\mathrm{CO,Gas}}[\mathrm{mL}] = \frac{Vol\%_{\mathrm{CO}}}{100} \cdot V_{Headspace} = \frac{1.2212}{100} \cdot 21\ \mathrm{mL} = 0.256\ \mathrm{mL}$$

$$n_{\mathrm{CO,Gas}}[\mu\mathrm{mol}] = \frac{p \cdot V_{\mathrm{CO}}}{R \cdot T} = \frac{1.45 \cdot 10^5\mathrm{Pa} \cdot 0.256\ \mathrm{mL}}{8.314\ \frac{\mathrm{J}}{\mathrm{K\cdot mol}} \cdot 293.15\ \mathrm{K}} = 15.3\ \mu\mathrm{mol}$$

Note: The headspace volume $V_{Headspace}$ is obtained by subtracting the solvent volume (here: 4.0 mL) from the maximum volume the reaction vial holds when filled completely. The pressure p includes the applied CO_2 overpressure for a total pressure of 1.45 bar.

$$p_{\mathrm{CO}}[\mathrm{mbar}] = \frac{n_{\mathrm{CO,Gas}} \cdot R \cdot T}{V_{Headspace}} = \frac{15.3\ \mu\mathrm{mol} \cdot 8.314\ \frac{\mathrm{J}}{\mathrm{K\cdot mol}} \cdot 293.15\ \mathrm{K}}{21\ \mathrm{mL}} = 18.0\ \mathrm{mbar}$$

$$\mathrm{c_{CO,Solv}}\left[\mathrm{mol_{CO}} \cdot \mathrm{mol_{MeCN}^{-1}}\right] = \frac{p_{\mathrm{CO}}}{K_{\mathrm{Henry}}} = \frac{18.0\ \mathrm{mbar}}{2507\ \mathrm{bar} \cdot \mathrm{mol_{MeCN}} \cdot \mathrm{mol_{CO}^{-1}}} = 7.18\ \mu\mathrm{mol_{CO}} \cdot \mathrm{mol_{MeCN}^{-1}}$$

$$\mathrm{n_{CO,Solv}}[\mu\mathrm{mol}] = \mathrm{c_{CO,Solv}} \cdot n_{\mathrm{MeCN}} = \mathrm{c_{CO,Solv}} \cdot \frac{V_{\mathrm{MeCN}}}{M_{\mathrm{MeCN}}} = 7.18\ \mu\mathrm{mol_{CO}} \cdot \mathrm{mol_{MeCN}^{-1}} \cdot \frac{4\ \mathrm{mL}}{41.05\ \mathrm{g} \cdot \mathrm{mol}^{-1}}$$
$$= 0.55\ \mu\mathrm{mol}$$

$$n_{\mathrm{CO,Total}}[\mu\mathrm{mol}] = n_{\mathrm{CO,Gas}}[\mu\mathrm{mol}] + \mathrm{n_{CO,Solv}}[\mu\mathrm{mol}] = 15.3\ \mu\mathrm{mol} + 0.55\ \mu\mathrm{mol} = 15.9\ \mu\mathrm{mol}$$

$$TON_{\mathrm{CO}} = \frac{n_{\mathrm{CO,Total}}[\mu\mathrm{mol}]}{n_{\mathrm{Re}}[\mu\mathrm{mol}]} = \frac{15.85\ \mu\mathrm{mol}}{0.00732\ \mu\mathrm{mol}} = 2159$$

Table S3: DFT calculated maximum molecule diameter of applied sacrificial electron donors and additive bases at the B3LYP/6-311G* level. Measured from the structures in Figure S14. With pKaH values of the conjugate acid of the additive bases.

Sacrificial electron donor	Maximum diameter [Å]	Additive base	Maximum diameter [Å]	pKaH value in MeCN[14]
BIH	10.62	DBN	6.84	28.9
BNAH	11.19	DBU	6.96	24.3
DMA	6.96	DIPEA	6.24	18.2
KEX	5.93			
Na Asc	7.09			
TEA	6.66			
TEOA	8.59			
TPP	9.70			

Table S4: First cycle TON values for the photocatalytic reduction of CO_2 to CO. Standard conditions: 0.5 mg ReRu-MIL (1320 nm) **or** homogeneous **1** (0.5 µmol) with **2** (4.0 µmol), 4 mL MeCN, 1.5 mmol sacrificial electron donor, 24 h, irradiation at 450 nm. The respective errors are calculated from averaging three repetitions under identical conditions and the catalyst quantity errors from ICP-MS analysis.

Sacrificial electron donor	TON (Homogeneous)	TON (ReRu-MIL (1320 nm))
TEOA	11.2 ± 0.3	9.2 ± 0.2
BIH	182 ± 12	344 ± 25
BNAH	0.5 ± 0.2	33.8 ± 0.7
DMA	0.8 ± 0.3	2.4 ± 0.1
KEX	7.6 ± 0.2	11.9 ± 0.3
Na Asc	11.1 ± 0.3	10.2 ± 0.2
TEA	3.3 ± 0.3	11.4 ± 0.3
TPP	0.9 ± 0.4	9.6 ± 0.2

Table S5: First cycle TON values for the photocatalytic reduction of CO_2 to CO. Standard conditions: 0.5 mg ReRu-MIL (1320 nm) **or** homogeneous **1** (0.5 µmol) with **2** (4.0 µmol), 4 mL MeCN, 0.2 mL TEOA (1.5 mmol), 0.15 mmol additive base, 24 h, irradiation at 450 nm. The respective errors are calculated from averaging three repetitions under identical conditions and the catalyst quantity errors from ICP-MS analysis.

Additive base	TON (ReRu-MIL (1320 nm))	TON (Homogeneous)
DBU	74.0 ± 1.8	51.5 ± 1.2
DBN	69.7 ± 1.7	18.0 ± 1.1
DIPEA	33.9 ± 1.7	37.0 ± 2.3
DBU/DBN/DIPEA without TEOA	n.-d.	n.-d.

Table S6: First cycle TON values for the photocatalytic reduction of CO_2 to CO. Standard conditions: 0.5 mg MOF, 4 mL MeCN, 1.5 mmol SED, 0.15 mmol additive base, 24 h, irradiation at 450 nm. The respective errors are calculated from averaging three repetitions under identical conditions and the catalyst quantity errors from ICP-MS analysis.

Particle size [nm]	SED	Base	TON
1320	BIH	DBU	971 ± 55
	BIH	None	314 ± 25
779	BIH	DBU	1218 ± 60
	BIH	None	374 ± 12
559	BIH	DBU	1679 ± 95
	BIH	None	435 ± 33
70	BIH	DBU	2159 ± 113
	BIH	None	509 ± 48
No MOF	BIH	DBU	n.-d.
1 (0.5 µmol) and **2** (4.0 µmol)	BIH	DBU	952 ± 66
	BIH	None	182 ± 15

Table S7: Recycling TON values for the photocatalytic reduction of CO_2 to CO after either adding 4.0 µmol **2** (homogeneous) or re-immobilizing further **2** (MOF assemblies). TON values provided are after 24 h under identical catalytic conditions to the first run respectively.

Sample	Cycle	SED	Base	TON
1 (0.5 µmol) and **2** (4.0 µmol)	2nd	BIH	None	n.-d.
1 (0.5 µmol) and **2** (4.0 µmol)	2nd	BIH	DBU	n.-d.
1 (0.5 µmol) and **2** (4.0 µmol)	2nd	TEOA	DBU	n.-d.
ReRu-MIL (1320 nm)	2nd	BIH	None	255 ± 14
	3rd			95 ± 12
	4th			11 ± 5
	5th			n.-d.
ReRu-MIL (559 nm)	2nd	BIH	DBU	798 ± 102
	3rd			408 ± 53
	4th			141 ± 20
ReRu-MIL (70 nm)	2nd	BIH	DBU	1221 ± 80
	3rd			649 ± 78
	4th			226 ± 88

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6. Atomic coordinates for DFT optimised molecules (B3LYP/6-311G*)

BIH (xyz coordinates in Angstroms)

C	-4.14540	0.69404	0.39726
C	-4.14541	-0.69403	0.39719
C	-2.95252	-1.41474	0.21220
C	-1.77672	-0.70420	0.04089
C	-1.77671	0.70422	0.04095
C	-2.95250	1.41475	0.21235
N	-0.45517	-1.14321	-0.11951
C	0.31587	0.00002	-0.62934
N	-0.45515	1.14322	-0.11940
C	-0.17206	2.44267	-0.69029
C	-0.17210	-2.44264	-0.69045
C	1.76254	-0.00001	-0.17257
H	0.30012	0.00007	-1.74509
C	2.80185	0.00014	-1.10233
C	4.13241	0.00013	-0.68117
C	4.42854	-0.00003	0.67832
C	3.39243	-0.00018	1.61483
C	2.06799	-0.00017	1.19238
H	-5.07640	1.23538	0.52961
H	-5.07642	-1.23537	0.52948
H	-2.96292	-2.49916	0.19929
H	-2.96288	2.49918	0.19955
H	0.90087	2.63397	-0.64261
H	-0.49968	2.52703	-1.73922
H	-0.67193	3.21860	-0.10868
H	0.90084	-2.63387	-0.64294
H	-0.67184	-3.21860	-0.10877
H	-0.49988	-2.52700	-1.73933
H	2.57055	0.00026	-2.16416
H	4.93273	0.00025	-1.41434
H	5.46192	-0.00003	1.01056
H	3.62117	-0.00031	2.67597
H	1.25666	-0.00029	1.91163

BNAH

C	-1.28855	2.21409	0.43519
C	-0.20816	1.68485	-0.14411
N	-0.17859	0.37605	-0.64172
C	-1.32922	-0.36565	-0.55935
C	-2.47317	0.06643	0.01440
C	-2.58017	1.45410	0.62431
C	-3.61015	-0.88407	0.00029
C	0.99522	-0.09771	-1.36701
C	2.25140	-0.20705	-0.51954
C	3.47840	0.23103	-1.02151

C	4.64615	0.09082	-0.27271
C	4.59583	-0.48563	0.99338
C	3.37329	-0.91960	1.50572
C	2.20983	-0.78104	0.75506
N	-4.77216	-0.42620	0.58039
O	-3.56148	-1.99738	-0.51036
H	-3.41516	2.01497	0.17552
H	-2.82148	1.39915	1.70043
H	-1.23395	3.23633	0.79401
H	0.71672	2.23696	-0.25870
H	-1.30028	-1.36023	-0.98825
H	0.74031	-1.07720	-1.77971
H	1.18840	0.55686	-2.22567
H	3.52383	0.68562	-2.00763
H	5.59177	0.43779	-0.67701
H	5.50206	-0.59291	1.58072
H	3.32659	-1.36692	2.49355
H	1.26035	-1.11312	1.16272
H	-5.51215	-1.10194	0.68448
H	-4.78408	0.37126	1.19303

TEA

N	-0.00006	-0.29754	-0.01610
C	1.21670	-1.07995	0.20454
C	2.45973	-0.44640	-0.41793
C	-1.21691	-1.07975	0.20470
C	-2.45981	-0.44616	-0.41801
C	0.00009	0.99082	0.69869
C	0.00022	2.20254	-0.23508
H	1.06412	-2.06254	-0.25132
H	1.39631	-1.26213	1.28221
H	3.32793	-1.09735	-0.27913
H	2.70241	0.51922	0.03307
H	2.31208	-0.29005	-1.48933
H	-1.39658	-1.26156	1.28242
H	-1.06440	-2.06250	-0.25081
H	-3.32812	-1.09696	-0.27918
H	-2.31204	-0.29000	-1.48942
H	-2.70235	0.51958	0.03280
H	0.87177	1.04273	1.36326
H	-0.87160	1.04303	1.36323
H	-0.00032	3.13689	0.33678
H	-0.88004	2.19867	-0.88213
H	0.88115	2.19917	-0.88123

TEOA

N	-0.00009	-0.36012	-0.07851
C	-2.41929	-0.60386	0.42094

C	-1.22061	-1.10850	-0.37155
O	-3.51815	-1.44378	0.08137
C	2.41906	-0.60431	0.42091
C	1.22030	-1.10873	-0.37159
O	3.51776	-1.44446	0.08141
C	0.00038	2.07329	0.44944
C	0.00004	0.99944	-0.63231
O	0.00055	3.33502	-0.21157
H	-2.18537	-0.65472	1.49328
H	-2.63851	0.44367	0.17079
H	-1.47854	-1.09509	-1.44453
H	-1.06748	-2.15383	-0.09484
H	-4.29727	-1.13782	0.55656
H	2.63848	0.44316	0.17072
H	2.18510	-0.65509	1.49325
H	1.06698	-2.15404	-0.09493
H	1.47820	-1.09530	-1.44457
H	4.29698	-1.13849	0.55642
H	-0.88564	1.95639	1.08861
H	0.88649	1.95609	1.08844
H	0.87488	1.15797	-1.27372
H	-0.87498	1.15825	-1.27340
H	0.00068	4.03150	0.45284

TPP

P	0.00064	0.00037	-1.21345
C	1.62993	0.36228	-0.40578
C	2.42849	1.34904	-1.00254
C	3.67139	1.67997	-0.47044
C	4.14736	1.01399	0.65809
C	3.37066	0.02139	1.25090
C	2.11992	-0.30112	0.72555
C	-0.50081	-1.59168	-0.40587
C	-0.04156	-2.77634	-1.00022
C	-0.37733	-4.01840	-0.46919
C	-1.19667	-4.09822	0.65591
C	-1.67203	-2.92964	1.24615
C	-1.32540	-1.68492	0.72186
C	-1.12773	1.23015	-0.40621
C	-2.38007	1.43047	-1.00540
C	-3.28884	2.34068	-0.47325
C	-2.95231	3.08302	0.65776
C	-1.70562	2.90494	1.25282
C	-0.80020	1.98383	0.72742
H	2.07376	1.85943	-1.89345
H	4.27340	2.44941	-0.94372
H	5.12071	1.26347	1.06856
H	3.73683	-0.50515	2.12698

H	1.52596	-1.07580	1.19728
H	0.58148	-2.72399	-1.88854
H	-0.00898	-4.92422	-0.94064
H	-1.46802	-5.06608	1.06549
H	-2.31520	-2.98400	2.11919
H	-1.70307	-0.78372	1.19184
H	-2.64311	0.87022	-1.89812
H	-4.25510	2.47885	-0.94831
H	-3.65557	3.80068	1.06826
H	-1.43429	3.48345	2.13061
H	0.16659	1.85545	1.20116

Ascorbic Acid

O	0.20622	2.13003	-0.17625
C	-0.40236	0.93632	-0.17563
C	0.32061	-0.35118	-0.48152
C	1.42019	-0.77631	0.50909
O	2.04108	-1.96313	0.04308
C	2.50103	0.27948	0.70659
O	2.67471	1.03174	-0.51040
O	-0.69755	-1.37276	-0.43879
C	-1.89441	-0.78720	-0.08828
O	-2.92268	-1.39974	0.04190
C	-1.69173	0.64946	0.07259
O	-2.72145	1.46352	0.39487
H	1.13882	2.00764	-0.44723
H	0.74952	-0.35173	-1.48712
H	0.93725	-0.95350	1.48040
H	1.34739	-2.62038	-0.09755
H	2.21650	0.95845	1.51691
H	3.42564	-0.23500	0.97647
H	3.53158	1.47047	-0.50112
H	-3.50920	0.90336	0.46693

DBN

N	-0.23216	0.64689	-0.02619
C	0.97890	1.40909	0.19835
C	2.15230	0.61707	-0.38648
C	2.13645	-0.83126	0.12723
N	0.83114	-1.49291	0.06827
C	-0.19537	-0.73781	0.02216
C	-1.63046	-1.23267	0.04701
C	-2.46663	0.01887	-0.27661
C	-1.56751	1.17983	0.18560
H	0.88443	2.38632	-0.28732
H	1.13414	1.59660	1.27314
H	3.09914	1.10634	-0.13796
H	2.06332	0.61794	-1.47787

H	2.49228	-0.86374	1.16643
H	2.84775	-1.43261	-0.44799
H	-1.77639	-2.06101	-0.64679
H	-1.84815	-1.61138	1.05149
H	-3.44232	0.02752	0.21238
H	-2.63204	0.09409	-1.35464
H	-1.71921	2.09568	-0.39472
H	-1.74195	1.42764	1.24569

DBU

N	0.28006	0.59644	-0.52393
C	-0.95252	1.27911	-0.90273
C	-2.00779	1.34556	0.22363
C	-2.04991	0.07814	1.08820
C	-2.12289	-1.25188	0.32183
C	-0.96517	-1.52124	-0.68237
C	0.32913	-0.78375	-0.39431
N	1.35926	-1.47745	-0.06681
C	2.60293	-0.76344	0.19412
C	2.38135	0.64512	0.75031
C	1.44225	1.41385	-0.17491
H	-0.68598	2.28798	-1.22800
H	-1.38102	0.79258	-1.78235
H	-1.80478	2.20422	0.87372
H	-2.98736	1.53262	-0.23306
H	-1.16229	0.06037	1.72883
H	-2.90530	0.14137	1.76951
H	-3.07915	-1.32187	-0.20929
H	-2.13132	-2.05679	1.06299
H	-1.29139	-1.28483	-1.70054
H	-0.70805	-2.57931	-0.67942
H	3.19838	-1.35967	0.89245
H	3.19024	-0.70857	-0.73443
H	3.32577	1.18756	0.85859
H	1.93288	0.57090	1.74706
H	1.97500	1.72097	-1.08656
H	1.09488	2.33083	0.31317

DIPEA

N	-0.04408	-0.12414	0.11123
C	0.17707	-1.35004	-0.67645
C	0.03325	-2.63786	0.13962
C	1.15790	0.72591	0.24575
C	1.66244	1.35104	-1.07053
C	2.28141	-0.02174	0.97470
C	-1.29602	0.57507	-0.24576
C	-1.48935	1.88416	0.52982
C	-2.50846	-0.32957	0.02124

H	1.17536	-1.33121	-1.12307
H	-0.50915	-1.37740	-1.53232
H	0.19838	-3.51790	-0.49212
H	-0.96020	-2.72088	0.58481
H	0.75955	-2.66554	0.95522
H	0.87410	1.54588	0.90764
H	0.87751	1.92567	-1.56968
H	2.49766	2.03186	-0.87984
H	2.01569	0.59336	-1.77595
H	1.91516	-0.43079	1.91883
H	3.10767	0.66078	1.19322
H	2.69133	-0.84575	0.38428
H	-1.30316	0.82421	-1.32498
H	-0.78131	2.66400	0.24434
H	-2.49063	2.27686	0.33652
H	-1.39902	1.71390	1.60693
H	-2.47319	-1.26127	-0.54519
H	-3.43145	0.18439	-0.26127
H	-2.56514	-0.58301	1.08367

DMA

N	-1.55552	-0.00001	0.00081
C	-0.16295	-0.00002	0.00032
C	0.58509	-1.19996	-0.00031
C	1.97486	-1.19159	-0.00044
C	2.69356	0.00001	-0.00010
C	1.97483	1.19159	0.00030
C	0.58506	1.19994	0.00045
C	-2.36538	1.20095	-0.00098
C	-2.36544	-1.20093	0.00044
H	0.09230	-2.16248	-0.00095
H	2.49888	-2.14300	-0.00093
H	3.77794	0.00002	-0.00027
H	2.49884	2.14301	0.00048
H	0.09225	2.16245	0.00076
H	-1.76575	2.10404	0.00051
H	-3.01255	1.23289	-0.88801
H	-3.01631	1.23257	0.88325
H	-1.76587	-2.10405	0.00533
H	-3.01783	-1.23028	0.88366
H	-3.01114	-1.23507	-0.88758

KEX

O	0.65968	-0.59921	0.00000
C	-0.59901	-0.17194	-0.00004
S	-1.85069	-1.23507	0.00000
S	-0.78295	1.61783	-0.00000
C	1.79418	0.30577	-0.00001

C	3.04273	-0.54946	0.00002
H	1.74011	0.93836	0.89045
H	1.74012	0.93831	-0.89051
H	3.92914	0.08984	0.00000
H	3.07608	-1.18648	-0.88549
H	3.07607	-1.18643	0.88556