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Supplementary Information

Incorporation of an intact dimeric Zr_{12} oxo cluster from a molecular precursor in a new zirconium metal-organic framework

Andrey A. Bezrukov, Karl W. Törnroos, Erwan Le Roux and Pascal D. C. Dietzel*

Department of Chemistry, University of Bergen, Bergen, Norway

pascal.dietzel@uib.no

Materials and Methods

Zirconyl chloride octahydrate was purchased from Alfa Aesar. All other chemicals and solvents were purchased from Sigma-Aldrich and used as received without further purification. Tris(4-carboxyphenyl)phosphine (H_3tpp) was synthesized following the procedure described in the literature.[1] Manipulations under inert atmosphere were performed either in a glove box (MBraun) or using Schlenk line technique. Gases were purchased from Yara Praxair and were of purity 99.999% or higher.

Suitable crystals for diffraction experiments were mounted in a minimum amount of Parabar 10312 oil (Hampton Research) in a nylon loop. Intensity data was collected with a Bruker AXS TXS rotating anode system with an APEX II Pt^{135} CCD detector using graphite-monochromated Mo *Kα* radiation. Data collection and data processing were done using APEX2,[2] SAINT,[3] and SADABS[4] version 2012/1. The structure solution and final model refinement were performed using SHELXT[5] version 2014/4 and SHELXL[6] version 2017/1, respectively.

Topological analysis of structure **2** was performed using ToposPro.[7]

The NMR spectra of compounds were recorded at 298 K on a *Bruker*-BIOSPIN-AV500 (5 mm BBO, ^{1}H: 500.13 MHz). ^{1}H shifts are referenced to the internal solvent resonances and reported in *parts per million* (ppm) relative to tetramethylsilane.

Powder X-ray diffraction was carried out on a Bruker AXS D8 Advance diffractometer equipped with automatic multisampler. Data collection was performed using monochromatic Cu $K\alpha_1$ radiation in Bragg-Brentano geometry.

Variable temperature powder X-ray diffraction was carried out using synchrotron radiation at beamline BM01 of the Swiss-Norwegian Beamlines (SNBL) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France, using a custom experimental setup, adapted from literature,[8] and an incident X-ray wavelength of 0.67511 Å. The as-synthesized **2** was placed into a 0.5 mm glass capillary. Glass fibers were placed on the downstream side of the sample to prevent it from being blown out of the capillary. The glass capillary with the sample and glass fibers inside was glued to the sample holder. A flow of helium gas was applied through the capillary while the sample was heated using a hot air blower with a rate of 2 K min^{-1} during data collection. Intensity data were collected using a custom-made diffractometer equipped with a Pilatus 2M detector.[9] The raw images were integrated azimuthally with the *Bubble* tool to normal one-dimensional powder diffraction patterns.[9]

Pawley profile fits for powder X-ray diffraction data were performed using TOPAS 4.2.[10]

Infrared spectra were recorded on a Nicolet 380 FTIR spectrometer, equipped with an ATR unit, in the spectral range 4000-650 cm^{-1} at room temperature.

A Netzsch STA 449 F1 Jupiter instrument was used for simultaneous thermogravimetry and differential scanning calorimetry. Measurement was performed using a flow of O_2/Ar (20/80 mixture) and a heating rate of 2 K min^{-1}.

Gas adsorption measurements were carried out on a BELSORP-max instrument. Compound **2** was immersed in dichloromethane several times. It was then dried in a dynamic vacuum at 298 K

overnight. Samples were transferred into the glove box, where sample cells were filled and transferred to the instrument under inert atmosphere using quick seals.

Synthesis

*Synthesis of **1***

Zirconyl chloride octahydrate (1.16 g, 3.6 mmol) and *N*,*N*-dimethylformamide (DMF, 1.8 mL) were placed into a glass culture tube with screw cap (Schott, ~20 mL). The reaction mixture was stirred until reactants were dissolved completely. Acetic acid (7.95 mL) was added to the solution and the mixture was stirred for 5 minutes until a clear solution was observed. The tube was sealed with a screw cap and placed in an oven pre-heated to 383 K. After 1 day, the tube was taken out of the oven and allowed to cool to room temperature. Colourless crystals were filtered and washed with DMF:acetic acid mixture (1:1, 50 mL). Yield: 0.60 g (64 % based on Zr^{IV}). Elemental analysis of **1** washed consecutively three times with $CHCl_3$ (Found: C, 20.6; H, 3.3; N, 0.2. Calc. for $Zr_{12}O_8(OH)_8(CH_3COO)_{24}$: C, 20.8; H, 2.9; N, 0.0%) indicates the crystal solvent and traces of DMF attached to the substance were removed during the washing process.

Synthesis of UiO-67

Biphenyl-4,4'-dicarboxylic acid (H_2bpdc) (73 mg, 0.3 mmol) and DMF (1.75 mL) were placed into a glass culture tube with screw cap (Schott, ~6 mL). The reaction mixture was sonicated for one hour. **1** (69 mg, 0.022 mmol) was added to the tube and the reaction mixture was sonicated for 10 minutes. The tube was sealed with a screw cap and placed in an oven pre-heated to 383 K. The tube was taken out of the oven after 3 days and allowed to cool to room temperature. The solid product was filtered and washed with DMF (20 mL).

*Synthesis of **2***

Single crystals of **2** that were used for structure determination were synthesized using the following procedure:
Zirconyl chloride octahydrate (97 mg, 0.3 mmol) and DMF (1.75 mL) were placed into a glass culture tube with screw cap (Schott, ~6 mL). The reaction mixture was stirred until the reactants were dissolved completely. Acetic acid (2.65 mL) was added to the solution and the mixture was stirred for 5 minutes. A clear solution was observed. The tube was sealed with a screw cap and placed in an oven pre-heated to 383 K. The tube was taken out of the oven after 11 days and allowed to cool to room temperature. A clear solution was observed. Tris(4-carboxyphenyl)phosphine (H_3tpp) (20 mg, 0.05 mmol) was added to the solution and the reaction mixture was purged with Ar. Then the tube was sealed with a screw cap and sonicated for 30 minutes until a clear solution was observed. The tube was placed in an oven pre-heated to 383 K. The tube was taken out of the oven after 10 days and allowed to cool to room temperature, obtaining colourless crystals as product.

In order to decrease the synthesis duration to a reasonable time, bulk samples of **2** were synthesized using the following procedure:
Tris(4-carboxyphenyl)phosphine (79 mg, 0.2 mmol) and DMF (7 mL) were placed into a glass microwave vial with septum (Biotage, ~31 mL). The reaction mixture was stirred until reactants were dissolved completely. Acetic acid (10.6 mL) was added to the tube and the mixture was stirred for 5 minutes. A clear solution was observed. **1** (278 mg, 0.09 mmol) was added to the tube. The tube was

sealed with a septum, sonicated for one hour and placed in a pre-heated oven at 383 K for 3 days. The tube was taken out of the oven and allowed to cool to room temperature. The solid product was filtered and washed with DMF. Yield: 212 mg.

Table S1. Summary of MOF synthesis experiments

Entry number	Linker	Metal to linker ratio (mmol)	Solvent (amount)	Product
1	H_2bpdc	Zr_{12}:L =0.022:0.25	DMF (1.75 mL)	**UiO-67**
2	H_2bpdc	Zr_{12}:L =0.022:0.3	DMF (1.75 mL)	**UiO-67**
3	H_3tpp	Zr_{12}:L =0.018:0.2	DMF (3 mL)	No crystalline product
4	H_3tpp	Zr_{12}:L =0.022:0.05	DMF (1.75 mL) and acetic acid (2.65 mL)	**2**
5	H_3tpp	Zr_{12}:L =0.09:0.2	DMF (7 mL) and acetic acid (10.6 mL)	**2**

The Zr^{IV} source is precursor **1**. The reaction was performed at 383 K for 3 days.

Catalytic testing

The coupling reaction of styrene oxide (SO) and CO_2 was performed in a 30 mL stainless steel multicell Asynt reactor equipped with a magnetic stirring bar. The reactor was charged with as-synthesized **2** (6 mg), [*n*Bu_4N]Br (6 mg, 0.02 mmol), and SO (1.14 mL, 10 mmol). The reactor was pressurized with CO_2 to 4 bar and then heated to 363 K for 4 h. After cooling down and venting the reactor, an aliquot of the reaction mixture was collected and dissolved in $CDCl_3$ for determining the product yield by ^{1}H NMR spectroscopy.

Table S2. Crystallographic data for **1** and **2**.

	Compound 1	**Compound 2**
Empirical formula	C_{58} $H_{100.97}$ $O_{76.48}$ Zr_{12}	C_{86} H_{102} O_{72} P_2 Zr_{12}
Formula weight	3116.73	3444.25
Temperature	103(2) K	103(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions	*a* = 20.287(3) Å, *b* = 12.5914(18) Å, *c* = 20.241(3) Å, *α* = 90°, *β* = 100.188(2)°, *γ* = 90°	*a* = 12.2903(16) Å, *b* = 16.666(2) Å, *c* = 19.138(2) Å, *α* = 72.790(2)°, *β* = 80.540(2)°, *γ* = 74.886(2)°
Volume	5088.9(13) $Å^3$	3598.9(8) $Å^3$
Z	2	1
Density (calculated)	2.034 $Mg·m^{-3}$	1.589 $Mg·m^{-3}$
Absorption coefficient	1.291 mm^{-1}	0.941 mm^{-1}
***F*(000)**	3082	1704
Crystal size	0.249 x 0.167 x 0.088 mm^3	0.145 x 0.047 x 0.034 mm^3
Theta range for data collection	1.912 to 31.518°	1.918 to 26.045°
Index ranges	-29 <= *h* <= 29, -18 <= *k* <= 18, -29 <= *l* <= 29	-15 <= *h* <= 15, -20 <= *k* <= 20, -23 <= *l* <= 23
Reflections collected	92593	45275
Independent reflections	16932 [R(int) = 0.0542]	14174 [R(int) = 0.0664]
Completeness	to theta = 25.242°, 99.9 %	to theta = 25.242°, 99.9 %
Absorption correction	Numerical	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.6983	1.0000 and 0.6607
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	16932 / 1458 / 765	14174 / 0 / 786
Goodness-of-fit on F^2	1.048	1.059
Final *R* indices [I>2sigma(I)]	R1 = 0.0369, wR2 = 0.0995	R1 = 0.0470, wR2 = 0.1278
***R* indices (all data)**	R1 = 0.0487, wR2 = 0.1077	R1 = 0.0705, wR2 = 0.1389
Largest diff. peak and hole	2.664 and -2.141 $e·Å^{-3}$	3.000 and -0.906 $e·Å^{-3}$

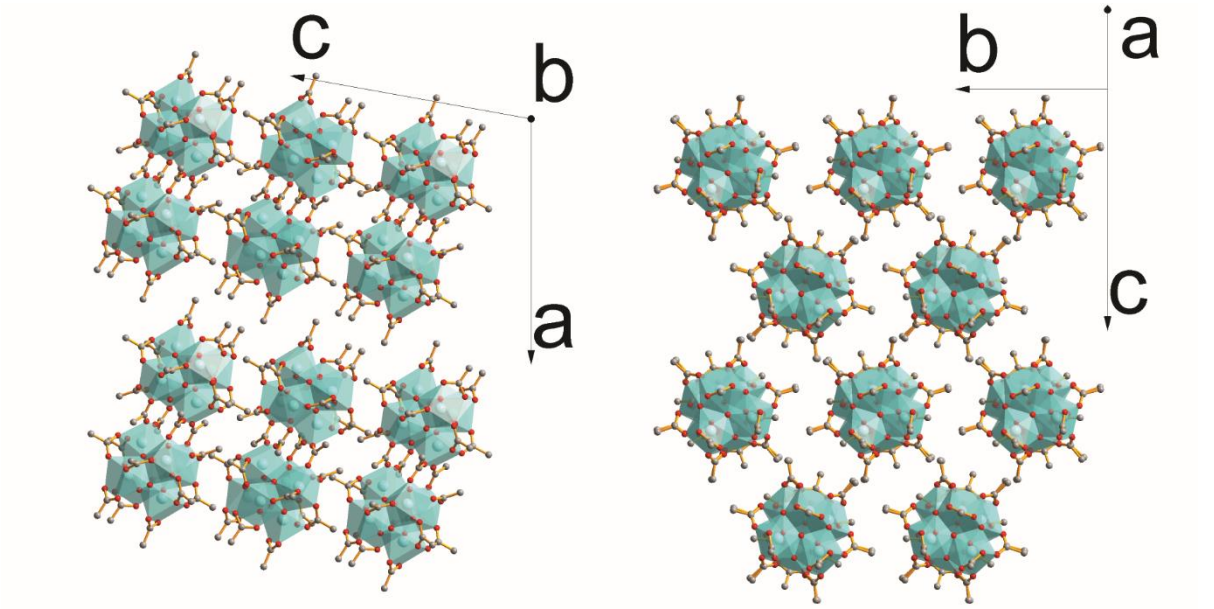

Figure S1. Packing arrangement of the dimeric $(Zr_6)_2$ oxo-clusters in the crystal structure of **1**. Solvent molecules and hydrogen atoms are omitted for clarity.

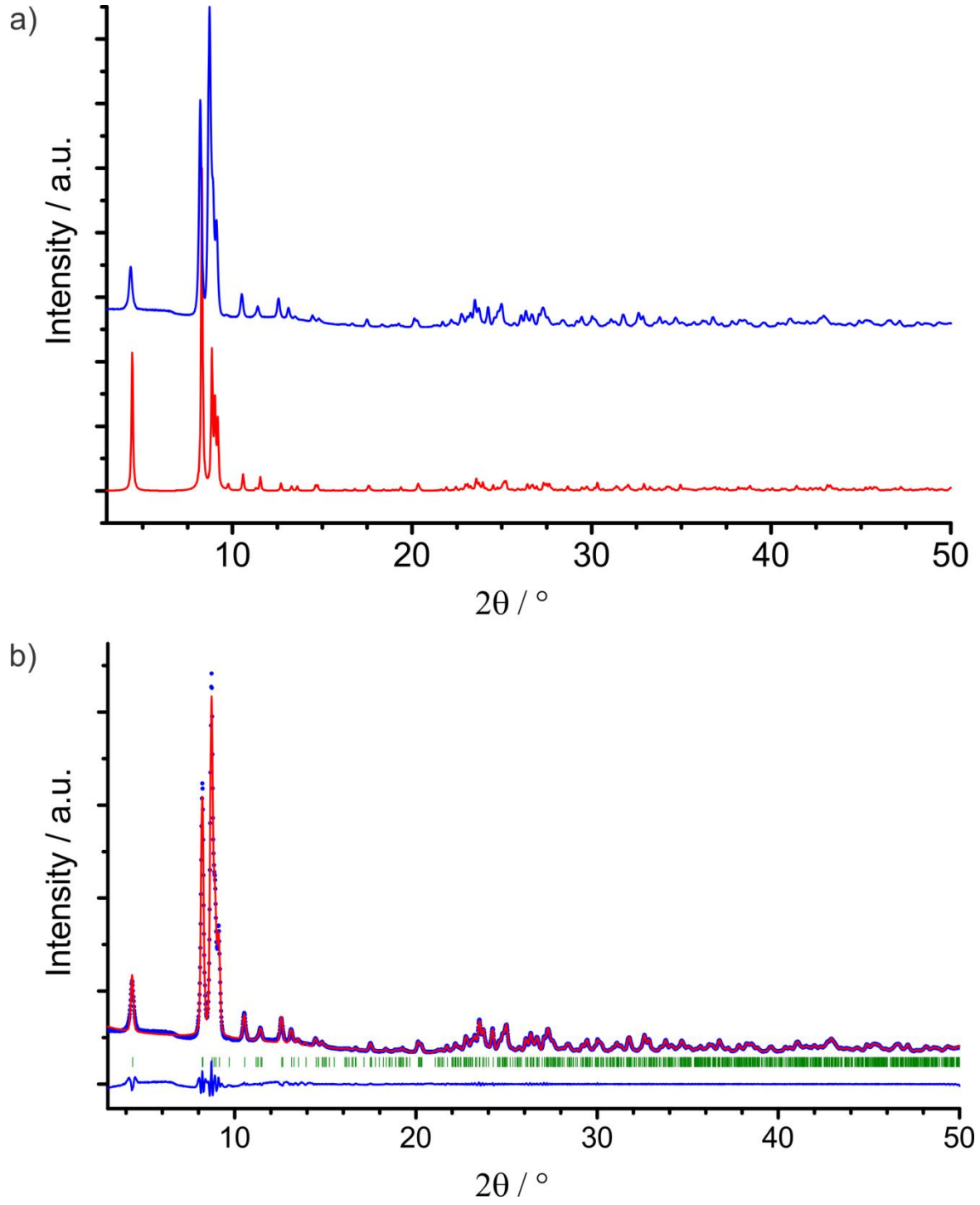

Figure S2. a) Powder X-ray diffraction patterns (λ = 1.5406 Å) of as-synthesized **1** measured in Bragg-Brentano geometry using a flat sample holder (blue) and calculated from the single crystal structure of **1** (red). b) Pawley profile fit of the powder X-ray diffraction pattern of as-synthesized **1** (Monoclinic $P2_1/c$, a = 20.527(3) Å, b = 12.699(3) Å, c = 20.278(3) Å, $\alpha = \gamma = 90°$, β = 100.30(17)°, V = 5201 (1.7) Å^3, R_p = 4.42, R_{wp} = 6.07).

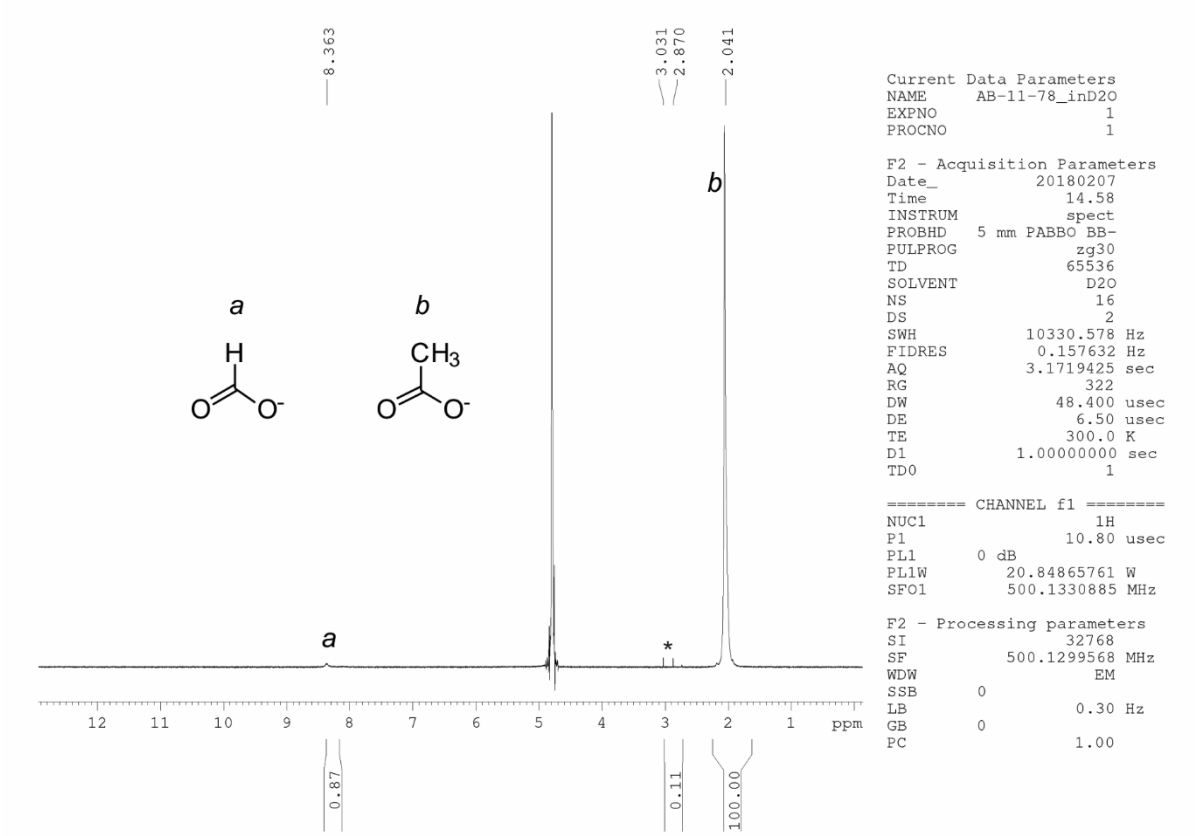

Figure S3. ^{1}H NMR spectrum of **1** washed once with $CHCl_3$ and dissolved in D_2O (* Two methyl groups from traces of DMF on the surface of **1**).

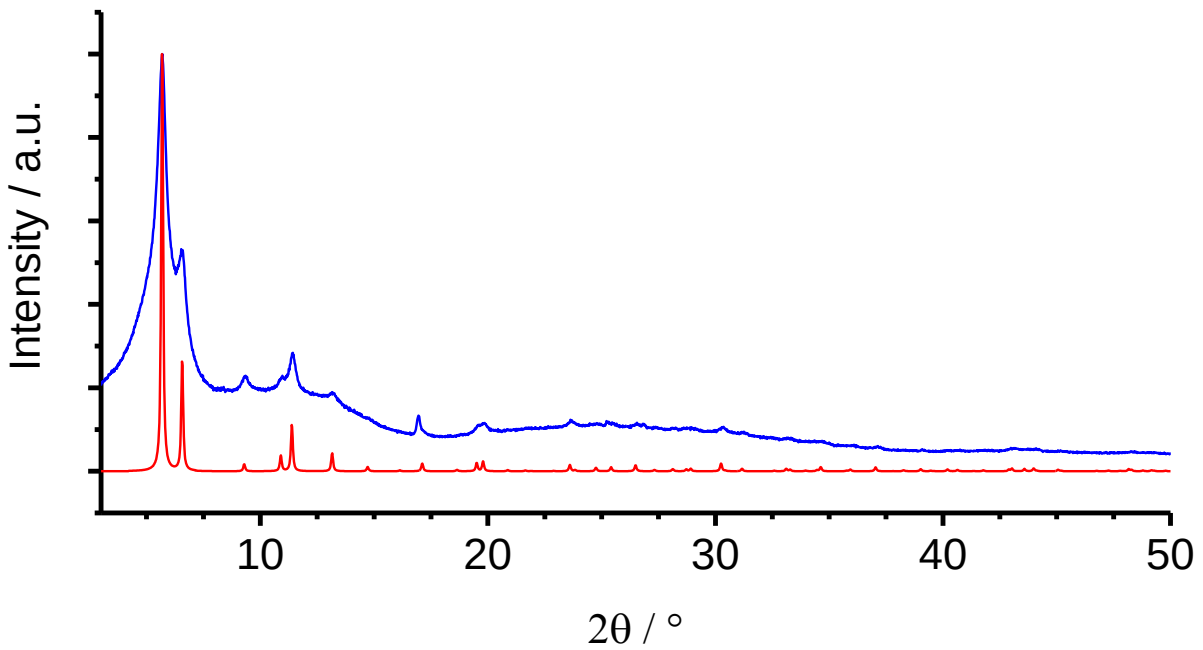

Figure S4. Powder X-ray diffraction patterns (λ = 1.5406 Å) of as-synthesized UiO-67 measured in Bragg-Brentano geometry using a flat sample holder (blue) and calculated from the single crystal structure of UiO-67[17] (red).

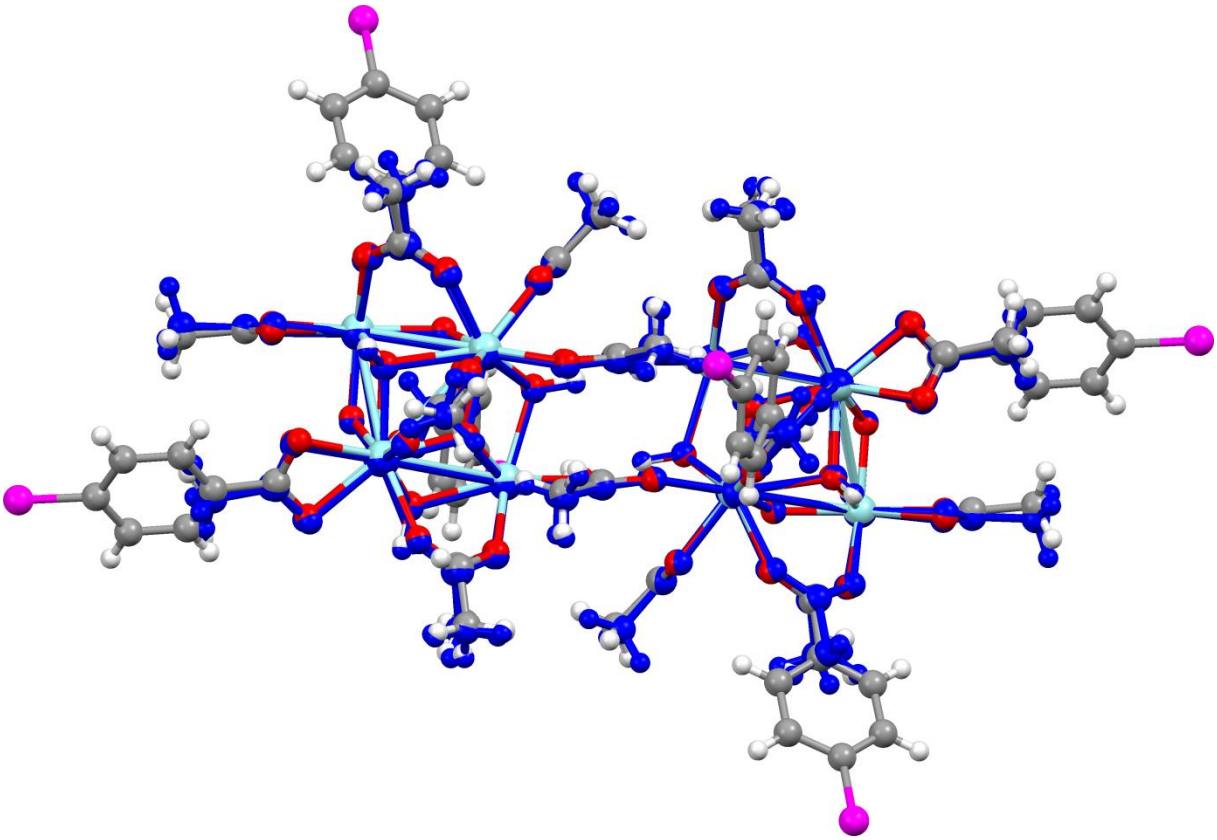

Figure S5. Overlay of the structure of the dimeric $(Zr_6)_2$ oxo clusters in the crystal structures of **1** (blue) and **2**.

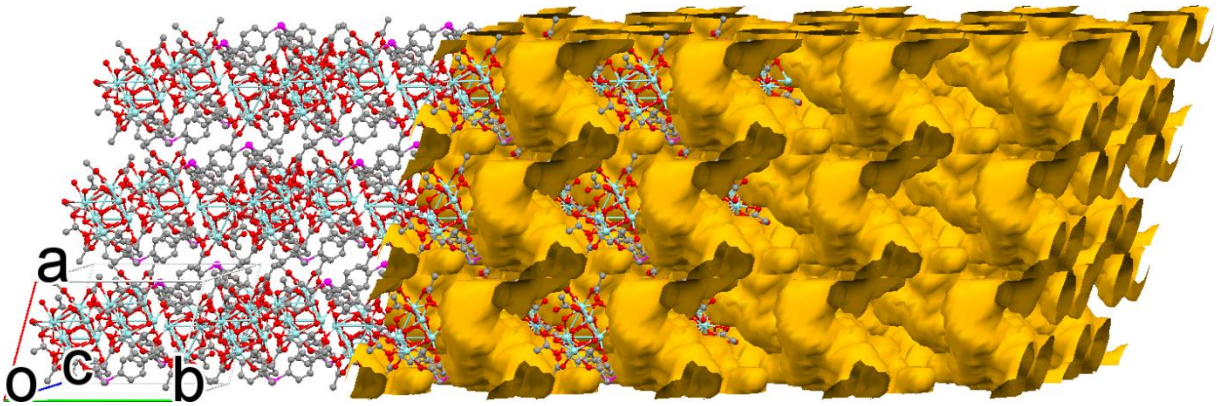

Figure S6. Illustration of the pore volume in the structure of **2** (calculated with Mercury, after deletion of crystal solvent from the crystallographic data). The layers of the 2D network in the structure of **2** are parallel to *bc* plane. The pore system is three-dimensional with the largest opening along [1$\bar{1}$0].

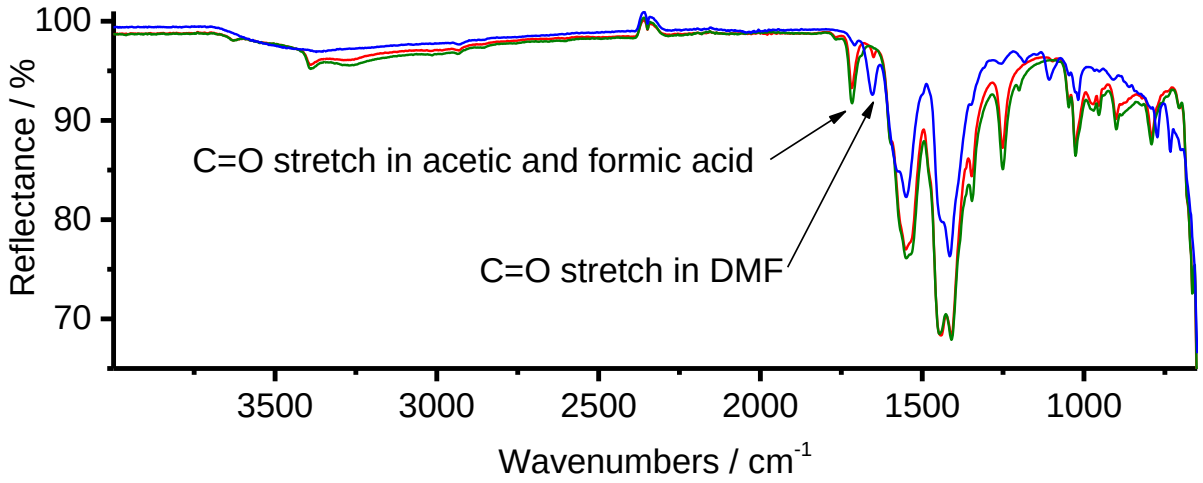

Figure S7. Infrared spectra of as-synthesized **1** (red) and **1** washed with $CHCl_3$ (green), showing that traces of DMF attached to as-synthesized **1** were removed during the washing procedure, and as-synthesized **2** (blue).

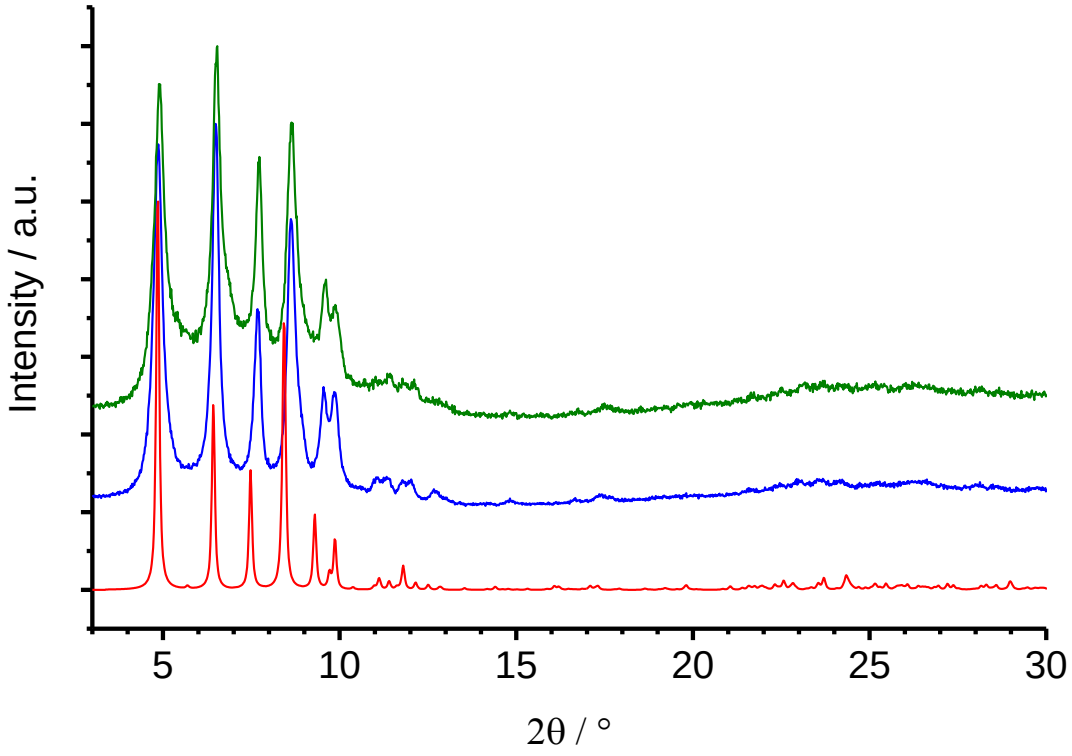

Figure S8. Powder X-ray diffraction patterns (λ = 1.5406 Å) of as-synthesized **2** covered with small amount of supernatant DMF (blue) and desolvated **2** (immersed in dichloromethane several times and subsequently heated under a dynamic vacuum at 363 K) covered with vacuum grease (green) measured in Bragg-Brentano geometry using a flat sample holder and calculated from the single crystal structure of **2** (red).

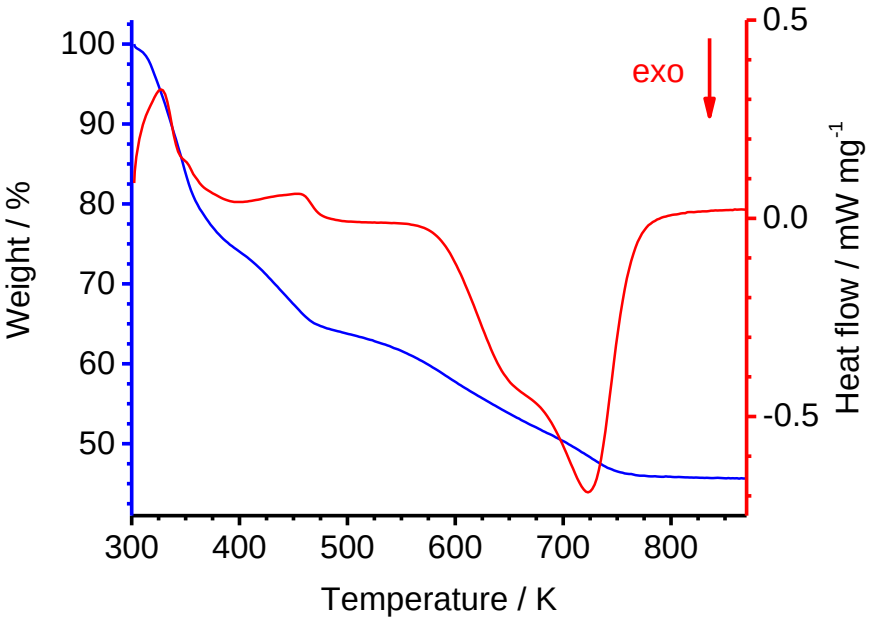

Figure S9. Simultaneous thermogravimetry (blue) and differential scanning calorimetry (red) of as-synthesized **2** in O_2/Ar (20/80) atmosphere.

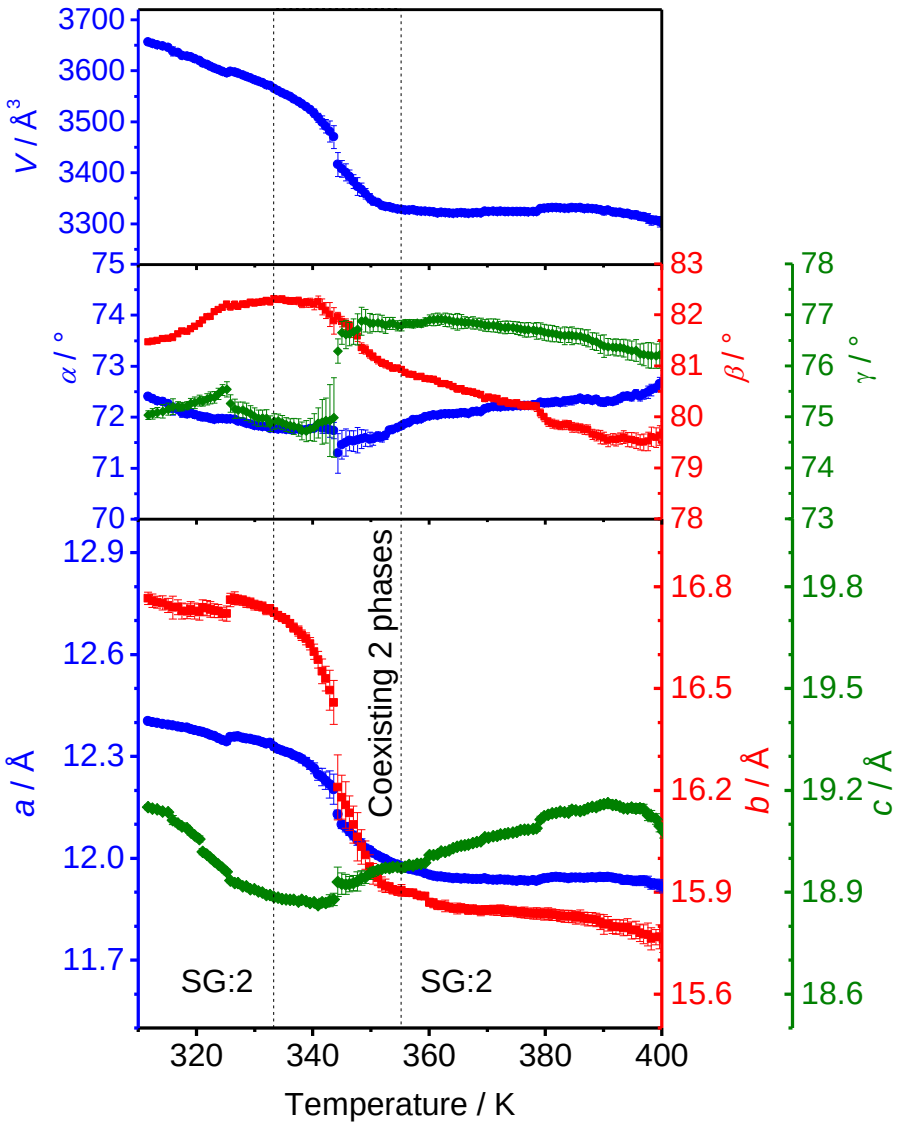

Figure S10. Evolution of lattice parameters as function of temperature. Lattice parameters were obtained from Pawley fits of synchrotron powder X-ray diffraction patterns (λ = 0.67511 Å) of as-synthesised **2** heated in helium flow.

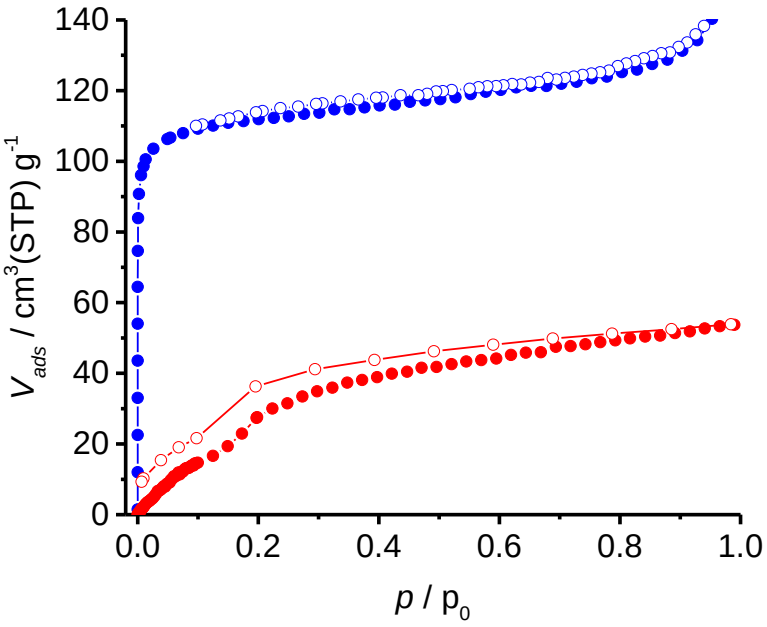

Figure S11. Sorption isotherms of nitrogen at 77 K (blue) and carbon dioxide at 278 K (red) for desolvated **2**. The adsorption branch is shown as closed symbols; the desorption branch is shown as open symbols.

Catalysis results

The chemical capture of CO_2 using catalytic coupling reactions with high-energy profile materials such as epoxides[11] is a promising route to obtain value-added cyclic carbonates.[12] Our initial studies show that **2** successfully catalyses the coupling of CO_2 and styrene oxide (SO) under neat conditions in the presence of [nBu$_4$N]Br as co-catalyst, and led selectively to styrene carbonate in 79% conversion (363 K, p_{CO_2} = 4 bar, 4 h, Fig. S12). Although the co-catalyst itself is effective in the CO_2 cycloaddition reactions to cyclic carbonates,[13] in our conditions the presence of both **2**/[nBu$_4$N]Br enhances the catalytic productivity (54 $g_{SC}{\cdot}g_{MOF}^{-1}{\cdot}h^{-1}$). This catalytic productivity of **2**/[nBu$_4$N]Br is similar the productivity of other MOF/[nBu$_4$N]Br systems (70 $g_{SC}{\cdot}g_{MOF}^{-1}{\cdot}h^{-1}$ for Cu-MOF,[14] 39 $g_{SC}{\cdot}g_{MOF}^{-1}{\cdot}h^{-1}$ for gea-MOF-1,[15] and 25 $g_{SC}{\cdot}g_{MOF}^{-1}{\cdot}h^{-1}$ for MIL-101-NH$_2$(Al)[16]), for which reaction conditions were actually at higher temperatures and pressure of CO_2 (Table S3).

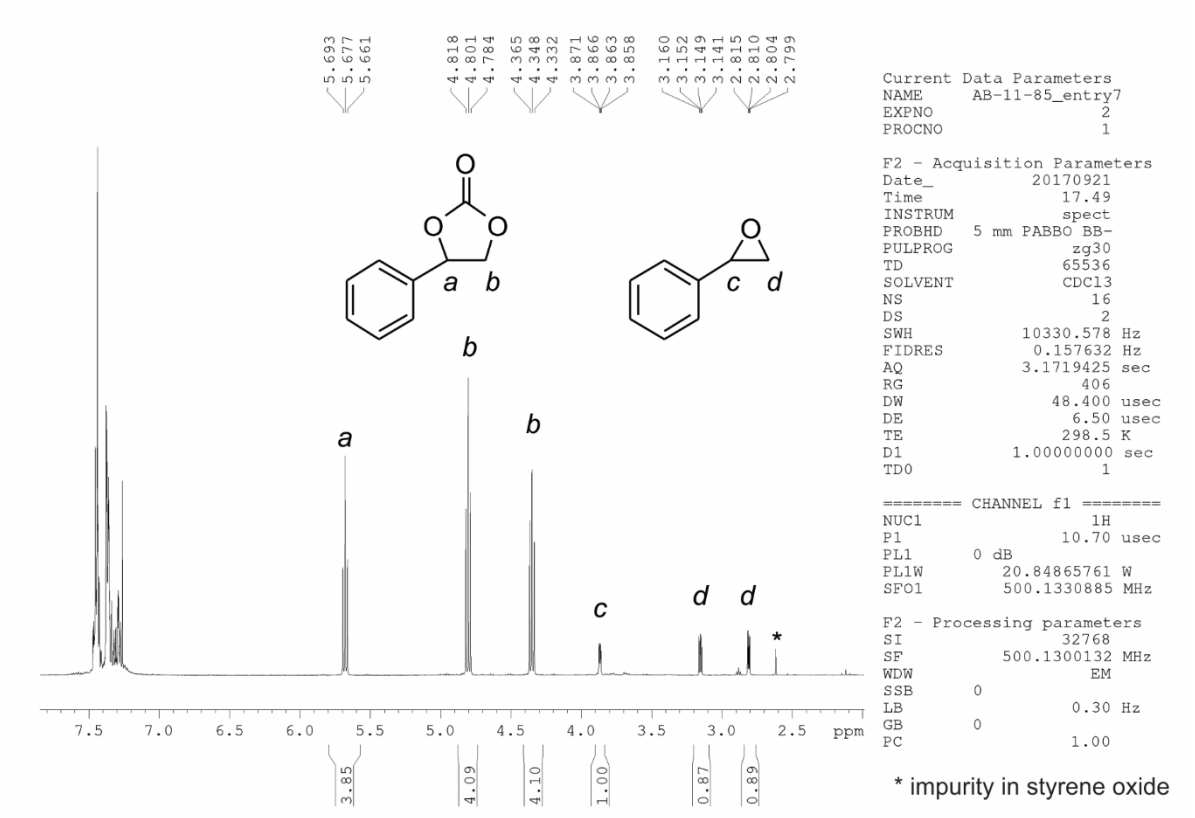

Figure S12. ^{1}H NMR spectrum of an aliquot from the reaction mixture of CO_2/styrene oxide coupling measured in $CDCl_3$. Conversion of styrene oxide was calculated using the following formula: n(styrene carbonate)/(n(styrene carbonate) + n(styrene oxide)) = a/(a+c).

Table S3. Comparison of known MOFs that catalyse the coupling of styrene oxide (SO) and CO_2 to styrene carbonate (SC) in the presence of [*n*Bu_4N]Br as the co-catalyst. MOFs in the table are sorted by the decrease of productivity.

Catalyst name	Catalyst mass / g	SO / mmol	[*n*Bu_4N]Br / mmol	T / K	P(CO_2) / bar	Time / h	Conversion / %	Productivity[b] /g_{SC} g_{MOF}^{-1} h^{-1}	Reference
Cu-MOF	0.005[a]	20	0.3	373	10	6	64.1	70	14
as-synthesized 2	0.006	10	0.02	363	4	4	79	54	**this work**
gea-MOF-1	0.060	100	0.15	393	20	6	85	39	15
MIL-101-NH_2(Al)	0.113[a]	105	0.15	393	18	6	99	25	16
as-synthesized PCN-700-Me2	0.0060	5.0	0.3	323	1	10	83.3	11	18
Ni(salphen)-MOF	0.05	10	0.3	353	20	4	81[c]	7	19
Zn-MOF	0.30[a]	25	0.125	373	20	6	99[c]	2.3	20
MOF-5	0.1	20	0.5	323	1	15	92[c]	2.0	21
Hf-NU-1000	0.0014[a]	0.2	0.02	328	1	13	100	1.8	22
MIL-101(Cr)	0.050	18	0.31	298	8	24	49	0.8	23
MOF-205	0.3[a]	42.8	0.3	298	12	24	58	0.6	24
UMCM-1-NH_2	0.3[a]	42.8	0.274	298	12	24	53	0.5	25

a: The mass of the MOF was calculated from the data reported in the corresponding article.
b: The productivity was calculated using the following formula: (mass(SC))/(mass(MOF)·time).
c: Only yield of SC was reported.

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