

Supporting Information

Unravelling the synthesis of a rare-earth cluster-based metal–organic framework with spn topology

Hudson A. Bicalho,^{†ab} Felix Saraci,^{†ab} Jose de J. Velazquez-Garcia,^c Hatem M. Titi,^d Ashlee J. Howarth^{ab*}

^a Department of Chemistry and Biochemistry, Concordia University, 7141 Sherbrooke St W., Montréal, QC, Canada

^b Centre for NanoScience Research, Concordia University, Montréal, QC, Canada

^c Photo Science - Structural Dynamics in Chemical Systems, Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, Hamburg, 22607, Germany

^d Department of Chemistry, McGill University, 801 Sherbrooke St W., Montréal, QC, Canada

***Corresponding author: Tel. +1 (514) 848-2424 ext. 5324**

E-mail: ashlee.howarth@concordia.ca

Experimental Procedures

S1. Materials

Prior to the reactions, *N,N*-dimethylformamide (DMF) was dried over 4A molecular sieves. All other chemicals were used as received. *N,N*-dimethylformamide (DMF), acetone, and hydrochloric acid were purchased from Fischer Scientific. Yttrium(III) nitrate hydrate and 1,3,5-benzenetricarboxylic acid (BTC) were purchased from Alfa Aesar. 2-fluorobenzoic acid (2-FBA) and 2,6-difluorobenzoic acid (2,6-dFBA) were purchased from Ambeed. Trifluoroacetic acid (TFA) was purchased from Sigma-Aldrich.

S2. Synthesis

Synthesis of Y-CU-45. In a 6-dram vial, $Y(NO_3)_3 \cdot xH_2O$ (118.5 mg, 0.31 mmol) and 2,6-dFBA (242 mg, 1.53 mmol) were mixed with 1.5 mL of dry DMF and 0.3 mL (3.92 mmol) TFA. This solution was sonicated for 20 minutes. Subsequently, BTC (13.5 mg, 0.065 mmol) was added to the solution. The mixture was sonicated once more until a homogeneous solution was obtained. The vial was then placed in a preheated oven at 130 °C and left undisturbed for 120 hours (5 days). The obtained light-yellow solid was collected and washed three times with DMF over the course of 24 h. Solvent exchanged was conducted by replacing DMF and washing the MOF three times with fresh acetone over the course of 24 h. Finally, the material was air dried and activated at 60 °C for 24 h under vacuum.

Acid-washed Y-CU-45. The same procedure described above was followed, except that after washing the solid three times with DMF, the material was soaked in 13 mL of DMF with 0.5 mL of

an aqueous solution of HCl (0.1 M) for 24 h. After that, the material was once again washed with DMF, followed by washing with acetone and finally activated at 60 °C for 24 h under vacuum.

As recently reported in the literature,¹ the F⁻ anions can act as bridging ligands in the rare-earth clusters, instead of oxo- and hydroxo-bridges which are often observed in metal clusters in MOFs. In a typical RE-MOF with 12-connected hexanuclear cluster nodes, the sum of charges would be negative, meaning that the MOF requires a positive counterion (usually dimethylammonium). Based on our detailed TGA, ICP-MS and NMR analysis herein, we have assigned a formula to Y-CU-45 that does not require negative counterions to balance the charge. In that way, it is unlikely that the F⁻ anions exist as extra framework species.

Y-CU-45 proposed formula (before acid washing): $[(\text{CH}_3)_2\text{NH}_2]_2[\text{Y}_6\text{X}_8(\text{BTC})_2(2,6\text{-dFBA})_3(\text{TFA})_2(\text{HCOO}^-)]$, X = OH⁻ or F⁻.

Y-CU-45 proposed formula (after acid washing): $\text{Y}_6\text{X}_8(\text{BTC})_2(2,6\text{-dFBA})_2(\text{TFA})(\text{HCOO}^-)$, X = OH⁻ or F⁻.

S3. Characterization

Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 Advance diffractometer with Ni-filtered CuK α radiation equipped with a LYNXEYE linear position sensitive detector (Bruker AXS, Madison, WI) over a range of $3 < \theta < 20^\circ$ at a scan rate of 2° min^{-1} .

Variable temperature powder X-ray diffraction (VT-PXRD) experiments were performed on a Bruker D8 Advance diffractometer equipped with Anton Paar CHC plus⁺ chamber. Diffractograms were collected in a stepwise fashion in a dry environment. After each collection (ca. 8 min), temperature in the chamber was raised by 5 °C at a rate of $1^\circ \text{ C min}^{-1}$ and a new collection started, in the range of 30 °C to 300 °C.

Scanning electron microscopy (SEM) images were recorded on a Phenom ProX Desktop instrument with accelerating voltage of 12 kV and using a ThermoScientific™ Phenom charge reduction sample holder.

Single-crystal X-ray diffraction experiments were performed in phi scan mode at 100 K, using a monochromatic X-ray beam with $\lambda = 0.6199 \text{ \AA}$ at P11 beamline in PETRA III, DESY, Hamburg, Germany. Crystal data and structure parameters are provided in Table SX. Data were processed using the XDS program package.^{2,3} Using Olex2,⁴ the structures were solved with the SHELXT⁵ structure solution program, and refined against F2 isotropically, followed by full matrix anisotropic least squares refinement by SHELXL.⁶ For all structures, hydrogen atoms were fixed geometrically, in idealized positions, and allowed to ride with the respective C or N atoms to which each was bonded, in the final cycle of refinement.

¹H and ¹⁹F-NMR spectroscopy data were collected on a 500 MHz Varian spectrometer and the chemical shifts were referenced to the residual solvent peaks. Prior to the analysis, the samples were digested by adding 8 drops of D₂SO₄ and 1 mL of DMSO-d₆, followed by sonication for 5 minutes.

Brunauer-Emmett-Teller (BET) apparent surface area measurements were determined by N₂ sorption isotherms collected at 77 K on a Micromeritics TriStar II Plus instrument. Prior to the analysis, the samples were washed with DMF and acetone, and then activated at 60 °C for 24 h using a Micromeritics Smart VacPrep (SVP) instrument equipped with a hybrid turbo vacuum pump.

Thermogravimetric analysis (TGA) coupled to Fourier-transform infrared (FT-IR) spectroscopy and gas chromatography–mass spectrometry (GC-MS) was performed on a PerkinElmer TGA 8000 / Spectrum Two FT-IR spectrometer / Clarus 690 gas chromatographer / Clarus SQ 8 C mass spectrometer hyphenated system. The TGA measurement was conducted under N₂

atmosphere, with a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ from 30 to $800\text{ }^{\circ}\text{C}$. New IR spectra were collected every 0.5 minute throughout the analysis. The GC column was kept at $250\text{ }^{\circ}\text{C}$ during the experiment, and the MS was set to electron ionization positive mode. Prior to the analysis, the samples were activated at $60\text{ }^{\circ}\text{C}$ for 24 h using the SVP.

Regular TGA analysis were carried out in a TGA 5500 equipment (TA Instruments) from 30 to $800\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under air. Prior to the analysis, the samples were activated at $60\text{ }^{\circ}\text{C}$ for 24 h using the SVP.

Inductively coupled plasma mass spectrometry (ICP-MS) measurements were collected on a 7500 Agilent 7500ce equipment. Prior to the analysis, a certain amount of MOF sample ($\sim 1\text{ mg}$) was added to 0.8 mL of concentrated HNO_3 and heated at $100\text{ }^{\circ}\text{C}$ for 1 h in a sand bath. After cooling down to room temperature, 0.2 mL of H_2O_2 (30 % w/w) was added to the mixture and heated at $100\text{ }^{\circ}\text{C}$ for another hour. Finally, the samples were sonicated for 10 minutes and the volume of the digested samples was adjusted to 10 mL using MilliQ water, and then further diluted 40 times. Prior to the analysis, the samples were activated at $60\text{ }^{\circ}\text{C}$ for 24 h using the SVP.

Y-CU-45 Characterization

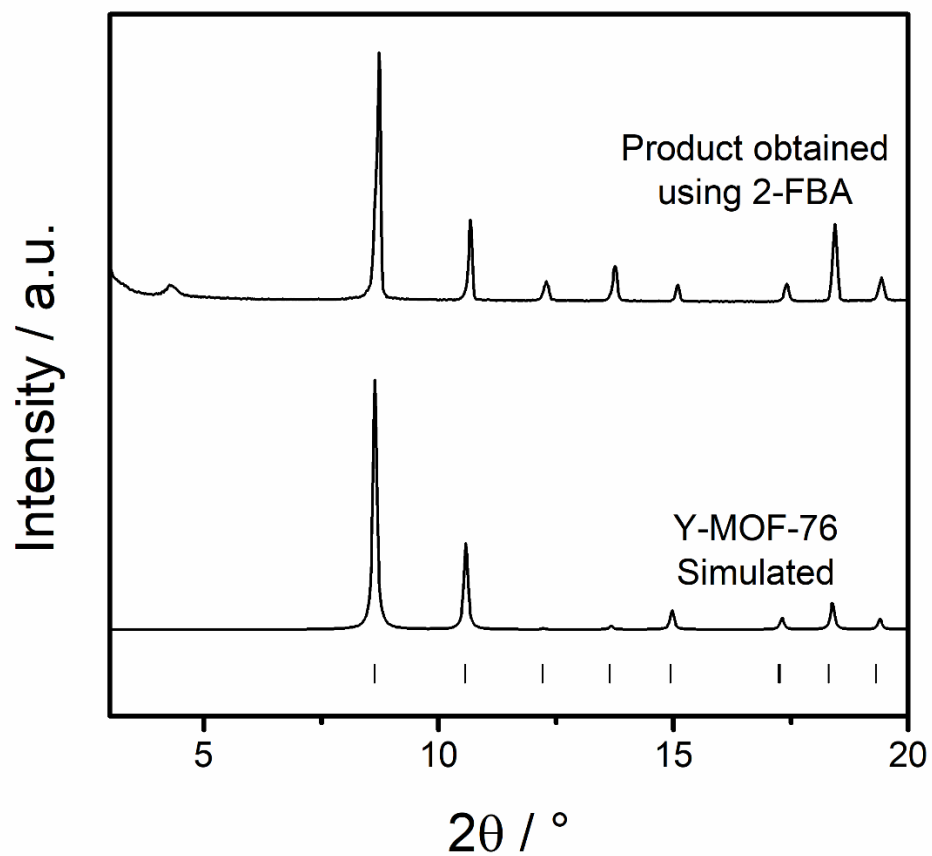


Figure S1. PXRD pattern of the simulated Y-MOF-76 and the product obtained using only 2-FBA as a modulator.

Reaction conditions: 0.31 mmol $Y(NO_3)_3 \cdot xH_2O$, 0.065 mmol BTC, 1.53 mmol 2-FBA, and 1.5 mL DMF heated at 130 °C for 120 hours.

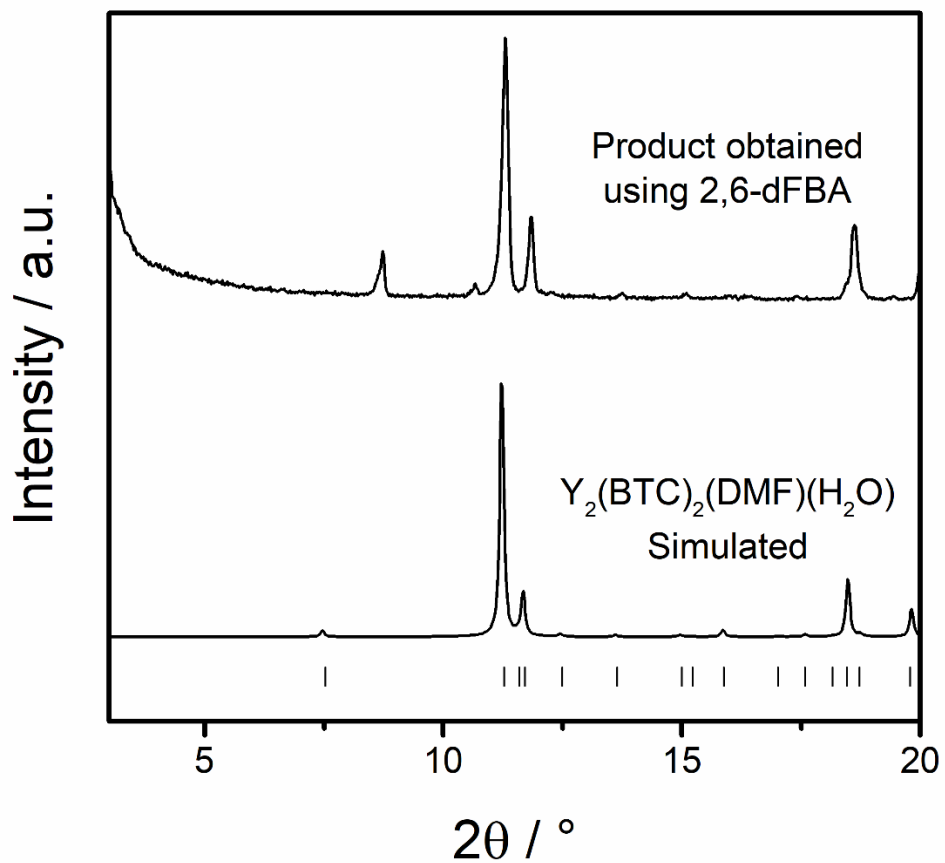


Figure S2. PXRD pattern of the simulated $\text{Y}_2(\text{BTC})_2(\text{DMF})(\text{H}_2\text{O})$ and the product obtained using 2,6-dFBA as a modulator.

Reaction conditions: 0.31 mmol $\text{Y}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, 0.065 mmol BTC, 1.53 mmol 2,6-dFBA, and 1.5 mL DMF heated at 130 °C for 120 hours.

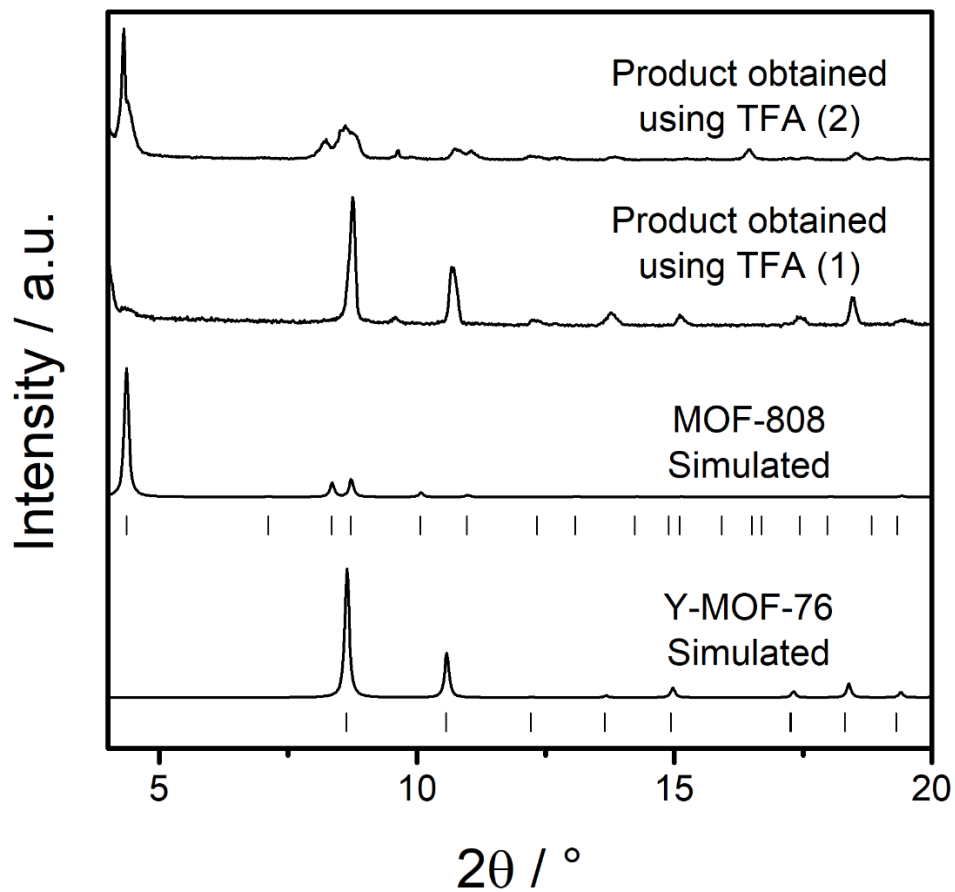


Figure S3. PXRD pattern of the simulated Y-MOF-76 and Zr-MOF-808 and the product obtained using TFA as a modulator, clearly showing a lack of reproducibility.

Reaction conditions: 0.31 mmol $\text{Y}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, 0.065 mmol BTC, 3.92 mmol TFA, and 1.5 mL DMF heated at 130 °C for 120 hours.

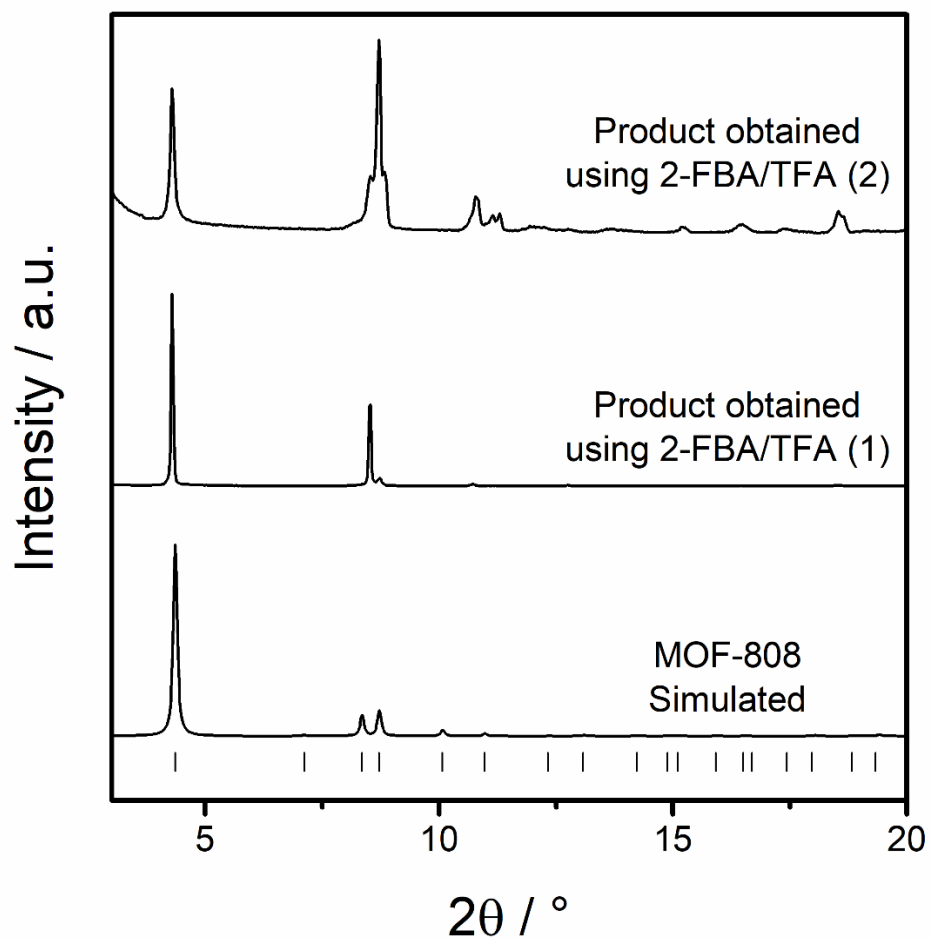


Figure S4. PXRD pattern of the simulated MOF-808 and the product obtained using 2-FBA/TFA as modulators, clearly showing the low reproducibility of results.

Reaction conditions: 0.31 mmol $Y(NO_3)_3 \cdot xH_2O$, 0.065 mmol BTC, 1.53 mmol 2-FBA, 3.92 mmol TFA, and 1.5 mL DMF heated at 130 °C for 120 hours.

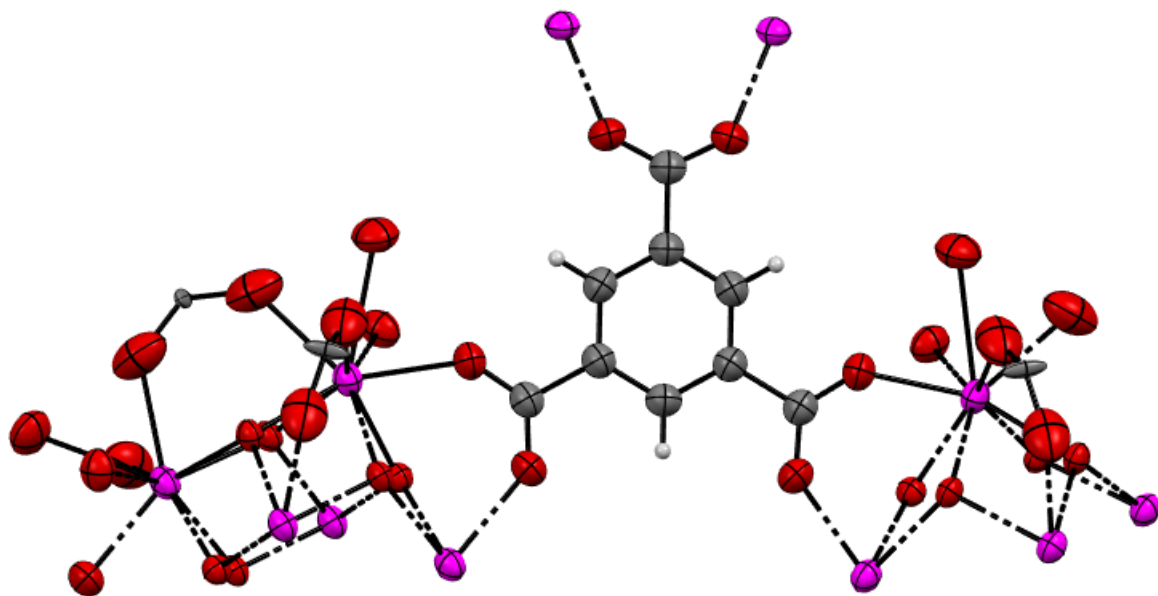


Figure S5. ORTEP diagram of the unit cell of Y-CU-45.

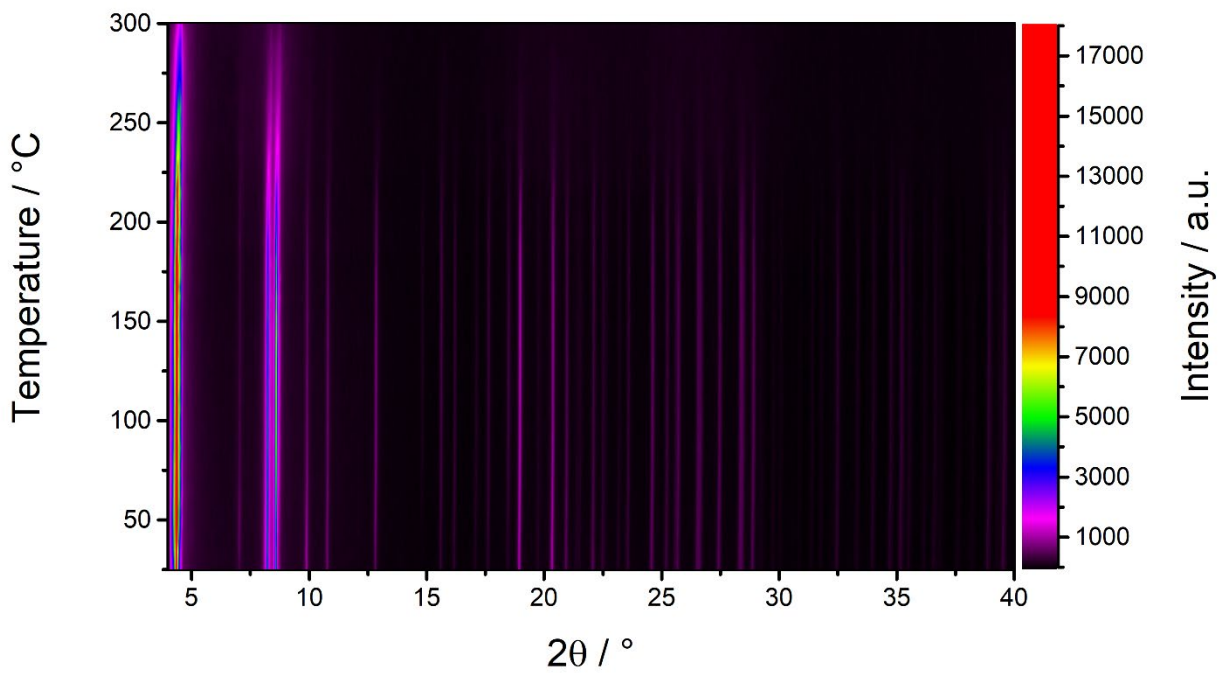


Figure S6. VT-PXRD of Y-CU-45 from 25 to 300 °C.

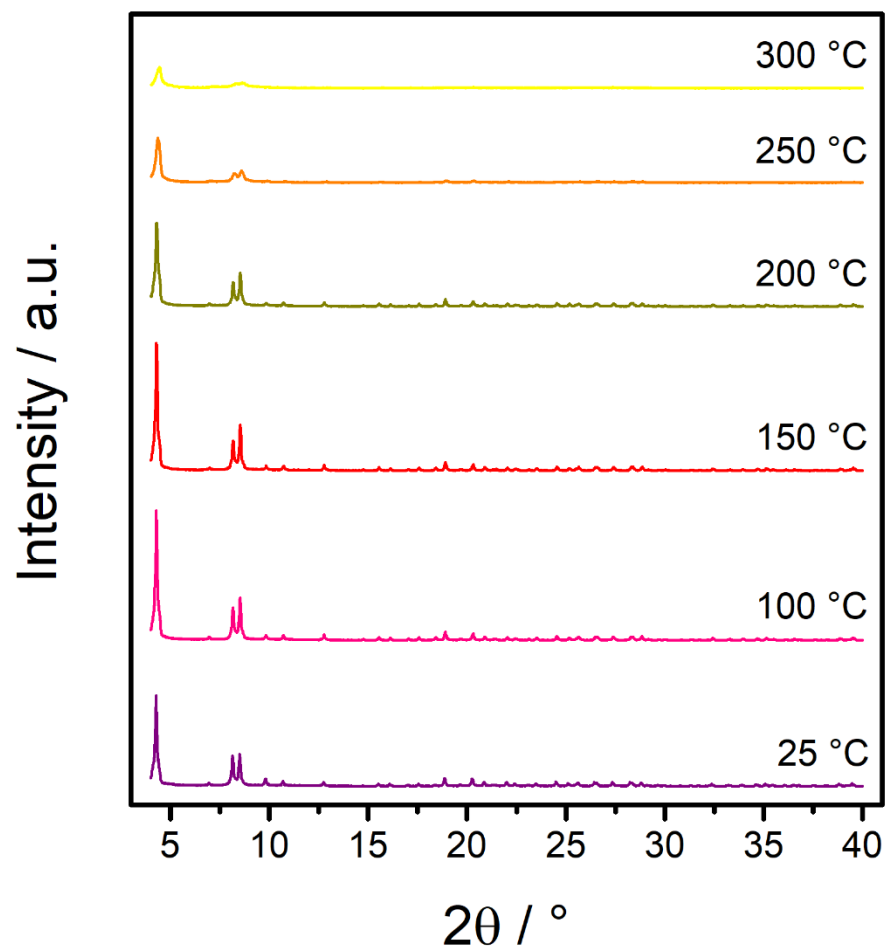


Figure S7. Non-normalized VT-PXRD patterns of Y-CU-45 at 25, 100, 150, 200, 250, and 300 °C.

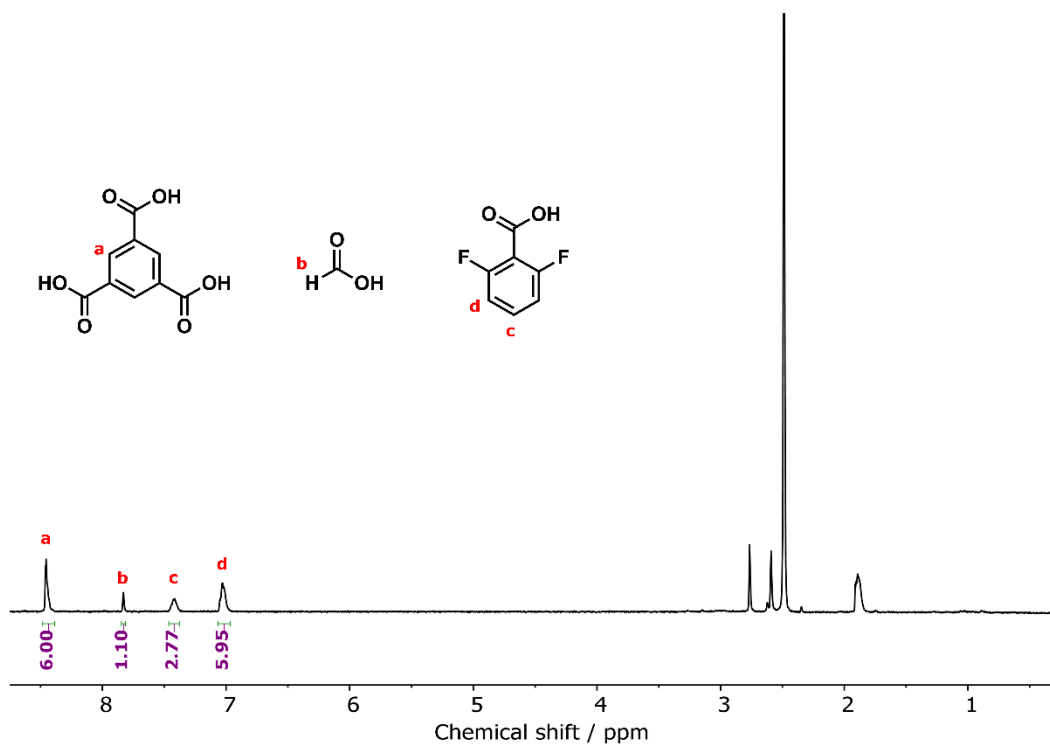


Figure S8. $^1\text{H-NMR}$ spectrum for Y-CU-45.

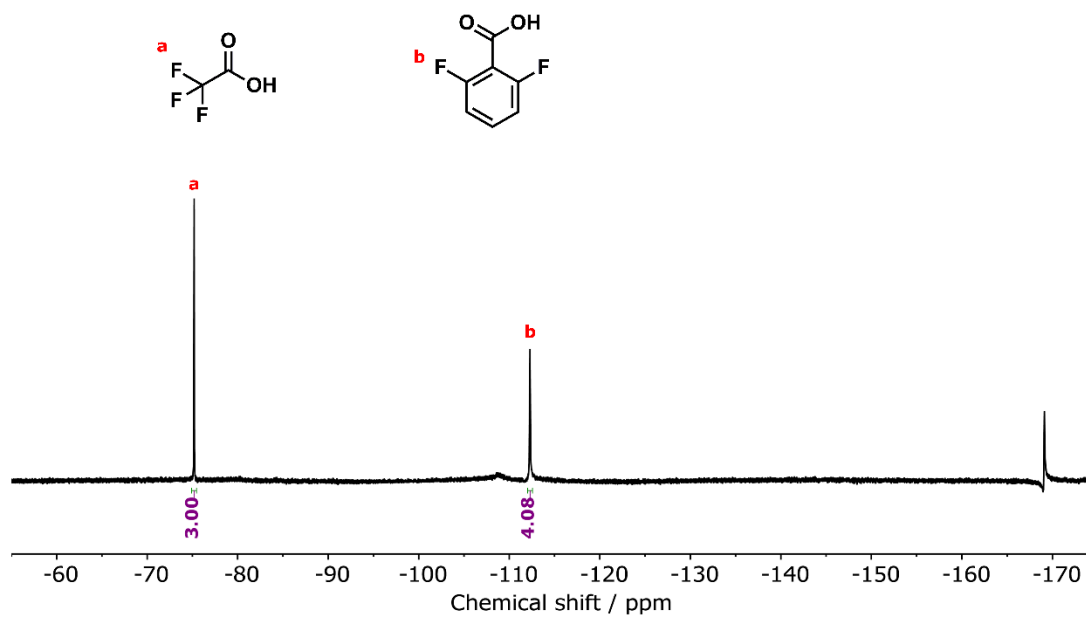


Figure S9. $^{19}\text{F-NMR}$ spectrum for Y-CU-45.

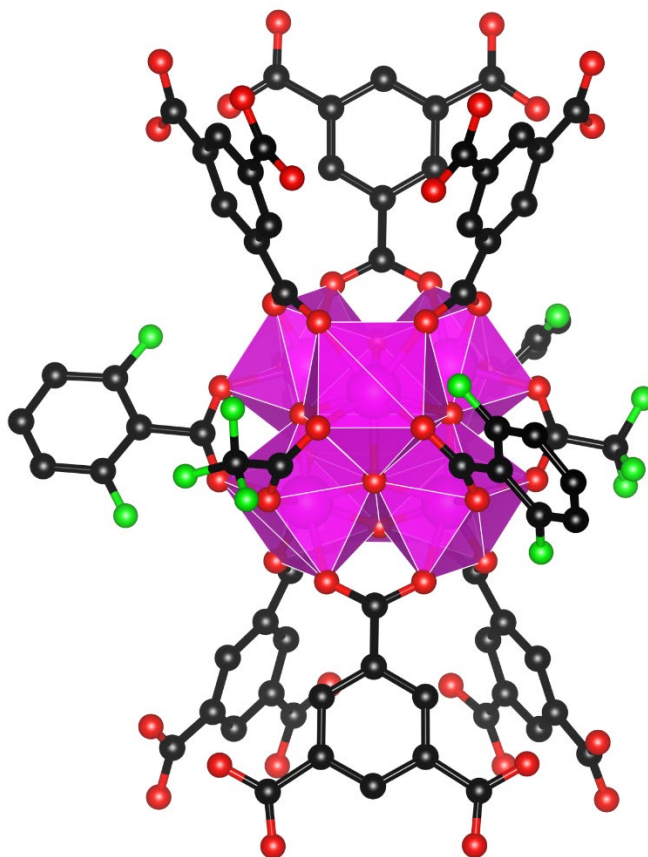


Figure S10. Hexanuclear Y(III)-cluster connected by six BTC linkers, three 2,6-dFBA, two TFA and one formate capping ligand. Overall charge of -2 may be balanced by dimethylammonium cations, dangling linkers, or missing linkers. Sphere colours: pink = yttrium, black = carbon, red = oxygen, green = fluorine.

Overall structure simulated on GaussView 6 and visualized on Vesta 3.

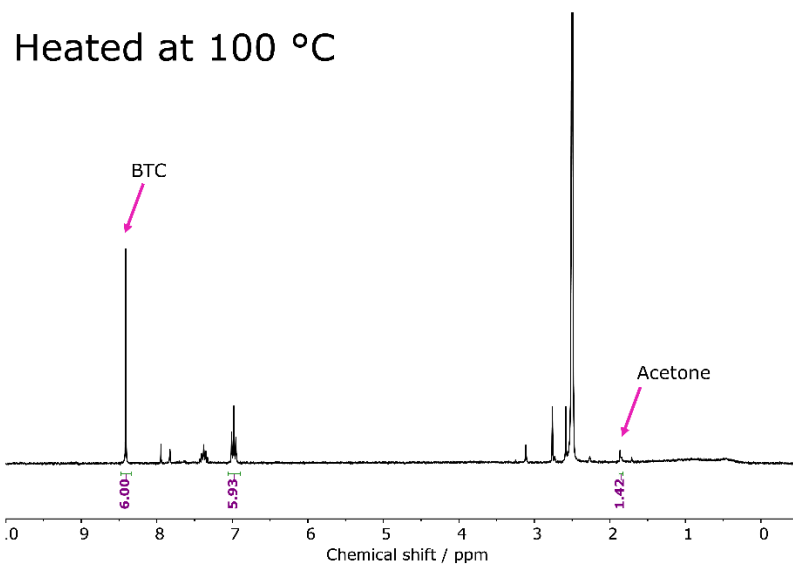
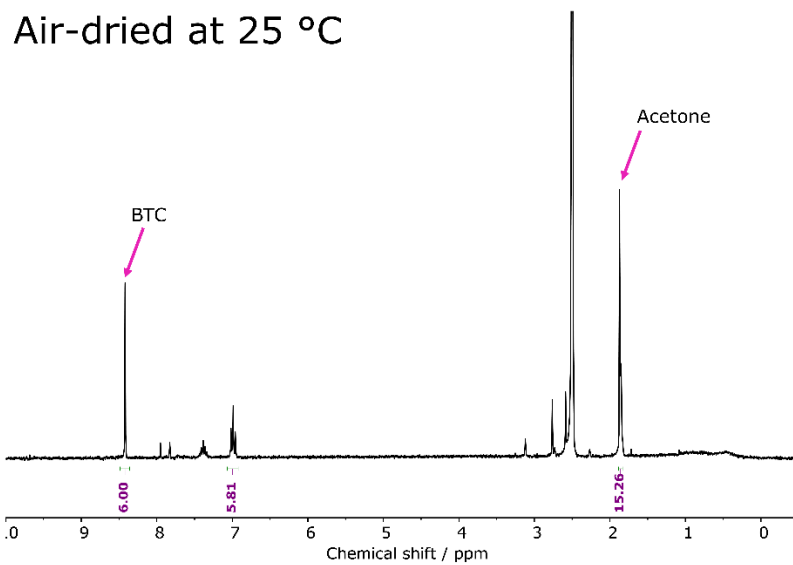


Figure S11. $^1\text{H-NMR}$ of an air-dried sample at 25 °C and a heated sample at 100 °C of Y-CU-45 demonstrating the loss of acetone upon heating.

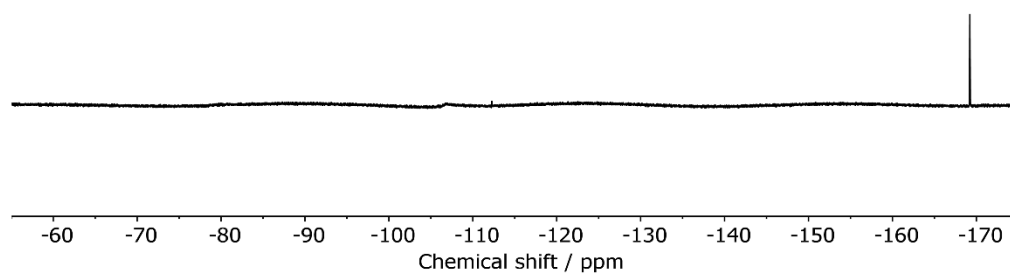


Figure S12. ^{19}F -NMR spectrum for Y-Uio-66.

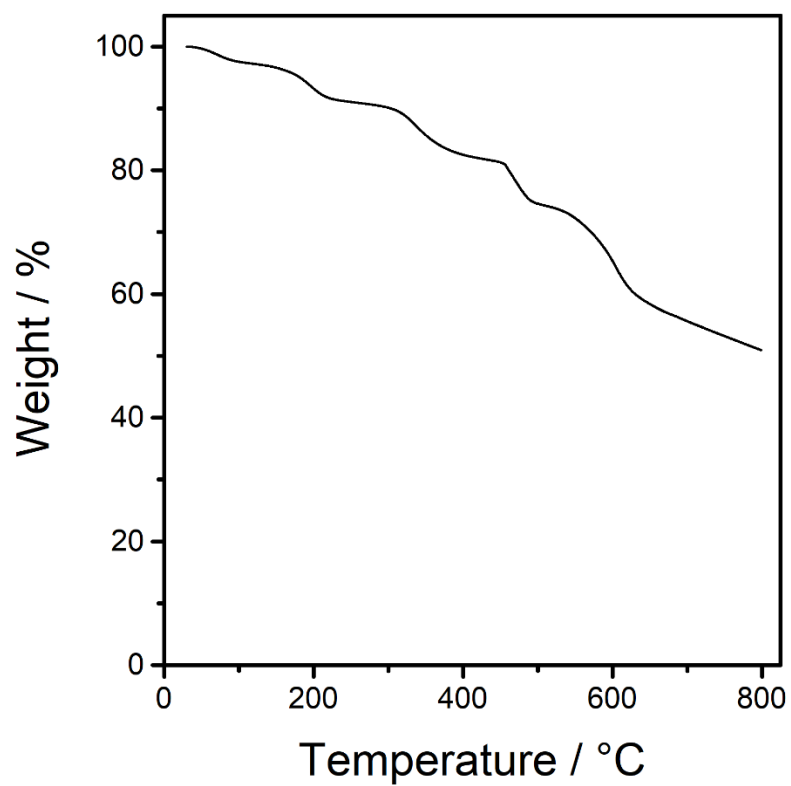


Fig. S13. TGA curve obtained during TGA-MS-IR experiment under N₂ atmosphere.

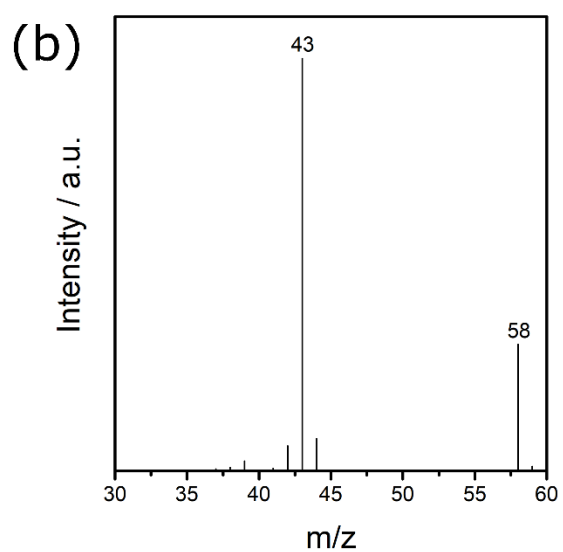
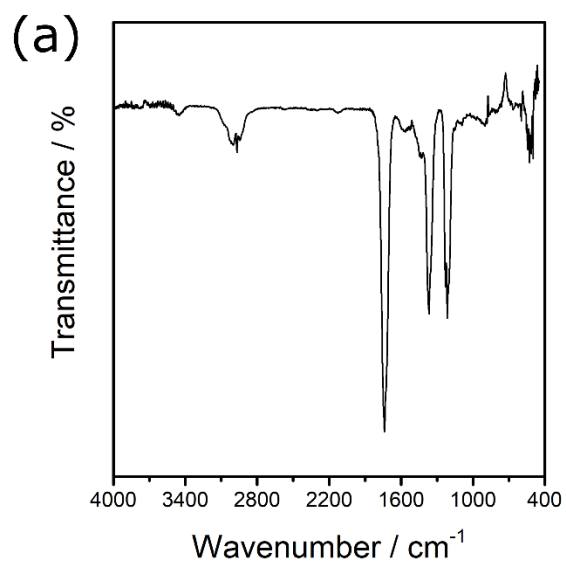


Figure S14. (a) IR and (b) MS spectrogram obtained during TGA-MS-IR experiment at 195 °C.

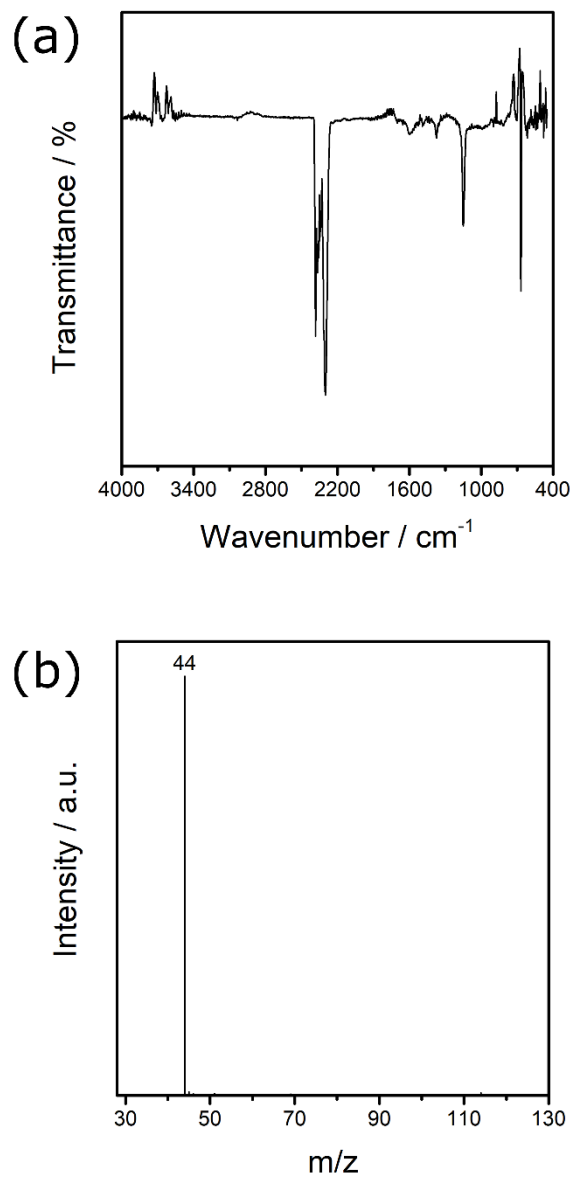


Figure S15. (a) IR and (b) MS spectrogram obtained during TGA-MS-IR experiment at 335 °C.

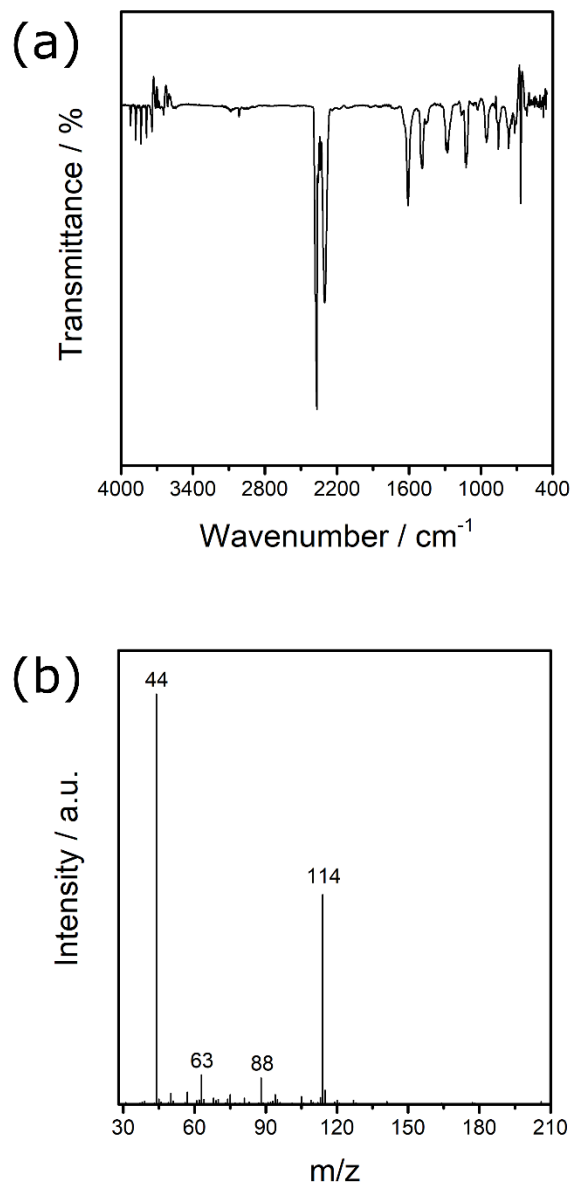


Figure S16. (a) IR and (b) MS spectrogram obtained during TGA-MS-IR experiment at 460 °C.

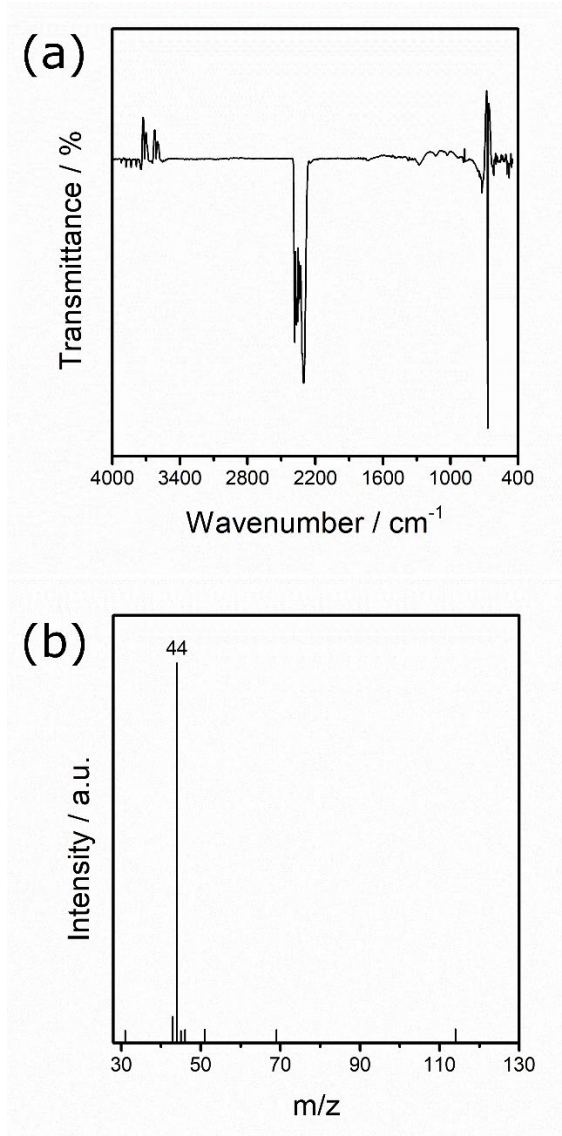
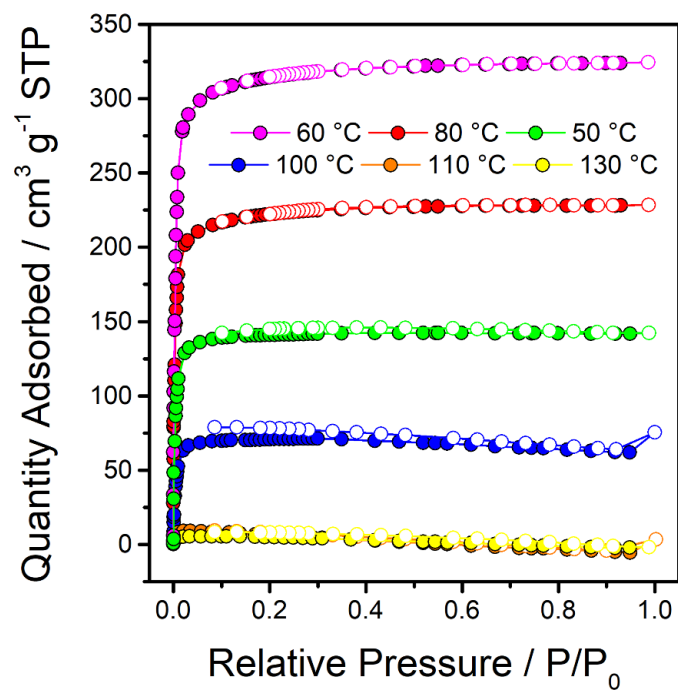


Figure S17. (a) IR and (b) MS spectrogram obtained during TGA-MS-IR experiment at 630 °C.



Temperature (°C)	S _{BET} (m ² g ⁻¹)
50	590
60	1280
80	880
100	300
110	40
130	20

Figure S18. N₂ sorption isotherms of Y-CU-45 samples activated for 24 h at different temperatures and the obtained BET areas.

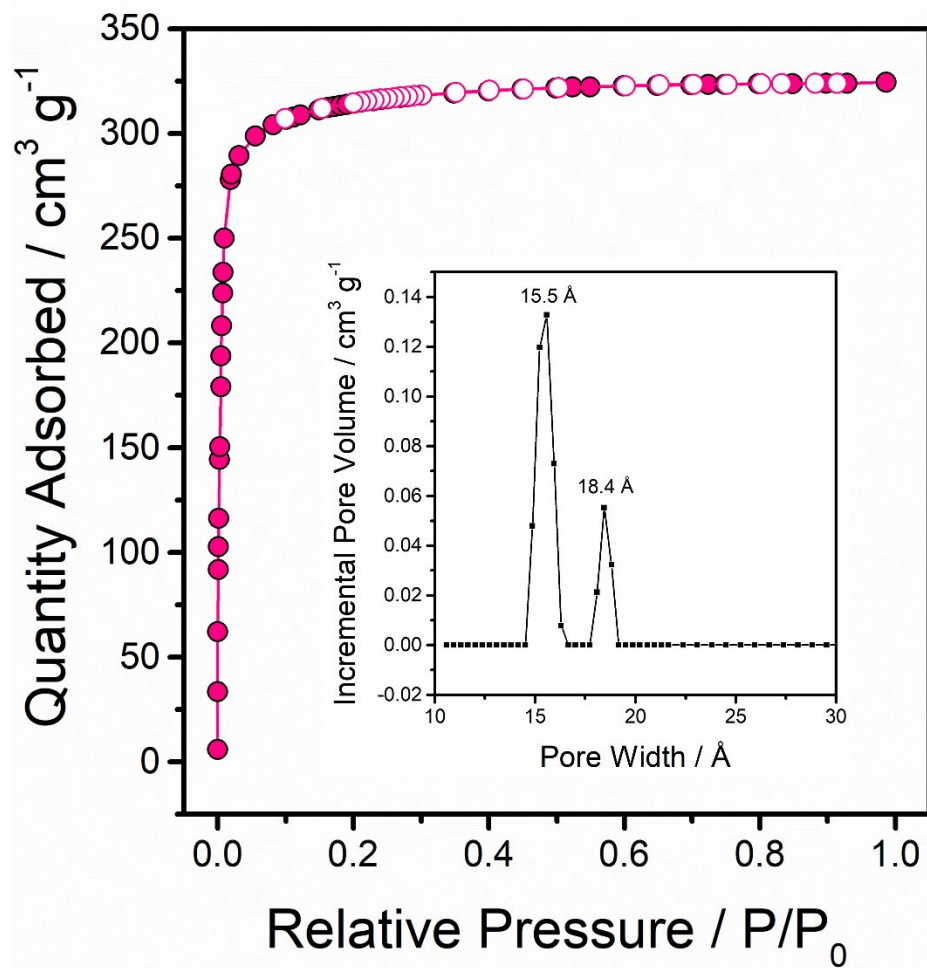
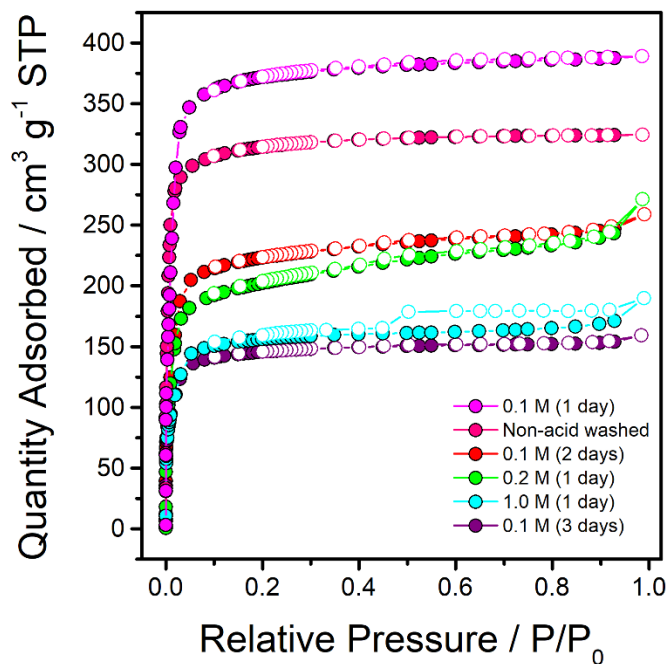


Figure S19. N₂ sorption isotherm of as-synthesized Y-CU-45 sample with inset of pore size distribution.



Acid washing condition	S_{BET} ($\text{m}^2 \text{g}^{-1}$)
Non-acid washed	1280
0.1 M (1 day)	1570
0.1 M (2 days)	870
0.1 M (3 days)	580
0.2 M (1 day)	800
1.0 M (1 day)	600

Figure S20. N_2 sorption isotherms of Y-CU-45 samples washed under different acidic conditions and the obtained BET surface areas.

After washing the solid three times with DMF, the material was soaked in 13 mL of DMF and 0.5 mL of an aqueous solution of HCl (0.1, 0.2, or 1.0 M) for 24 h. In some cases, the solution was exchanged by a new one every 24 h (for 2 and 3 days). After that, the material was once again washed with DMF, followed by washing with acetone and finally activated at 60 °C for 24 h under vacuum.

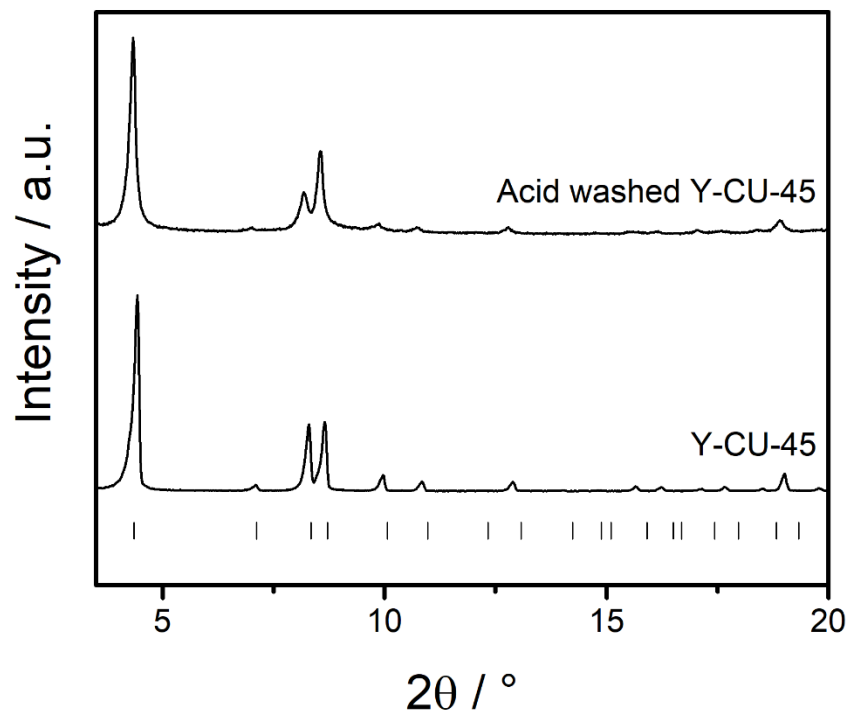


Figure S21. PXRD patterns of regular and acid washed Y-CU-45.

Table S1. ICP-MS data of digested non-acid washed and acid-washed Y-CU-45.

Sample	Mass (mg)	Concentration Y (ppm)	Concentration % Y by mass (%)
Non-acid washed Y-CU-45 (1)	0.498	14.34	28.80
Non-acid washed Y-CU-45 (2)	1.100	31.8	28.91
Acid washed Y-CU-45 (1)	0.827	25.11	30.36
Acid washed Y-CU-45 (2)	1.574	48.08	30.55

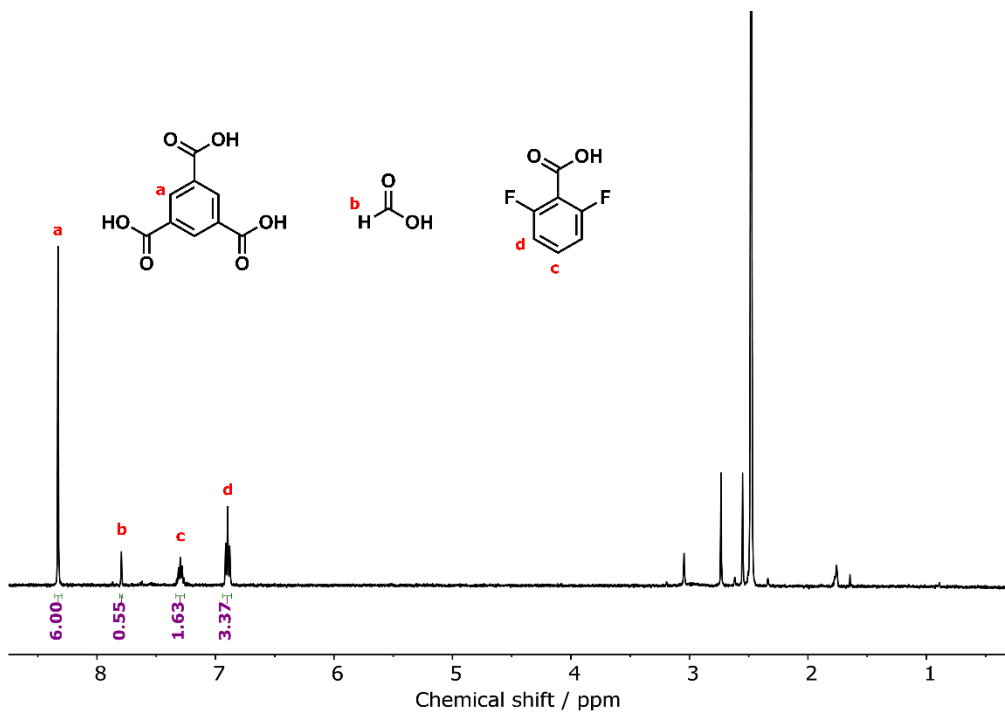


Figure S22. $^1\text{H-NMR}$ spectrum for Y-CU-45 washed with 0.1 M HCl for 1 day.

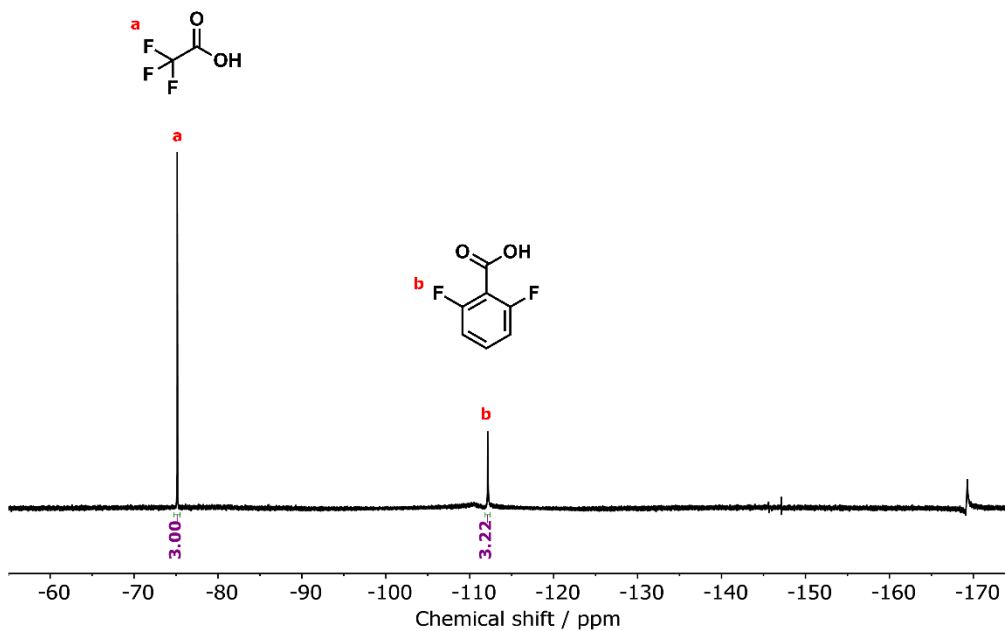


Figure S23. $^{19}\text{F-NMR}$ spectrum for Y-CU-45 washed with 0.1 M HCl for 1 day.

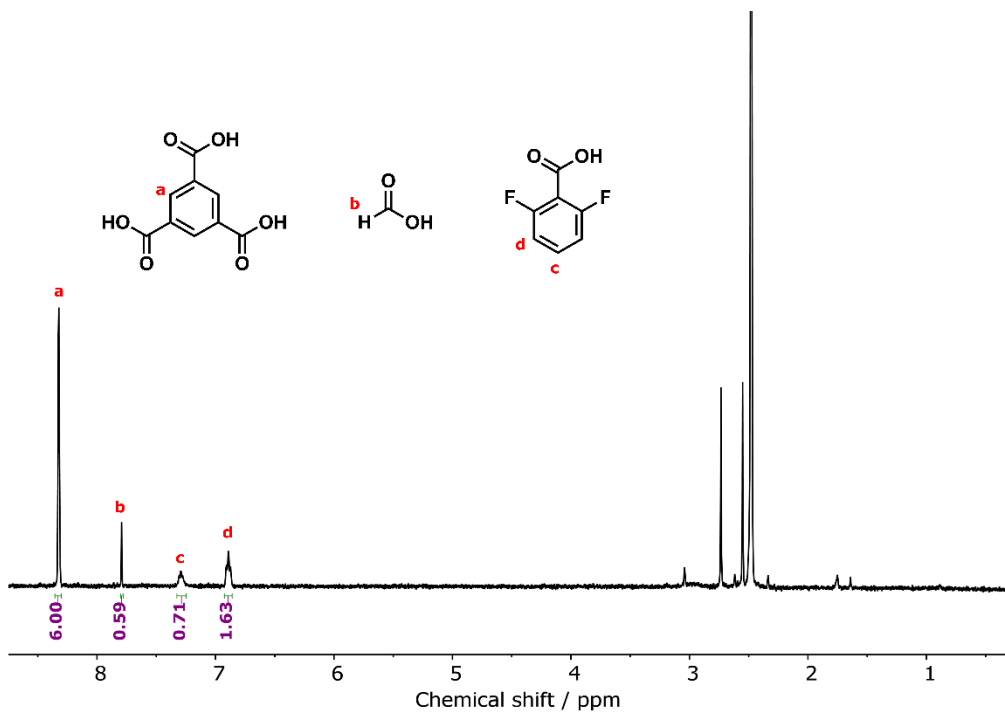


Figure S24. $^1\text{H-NMR}$ spectrum for Y-CU-45 washed with 0.1 M HCl for 2 days.

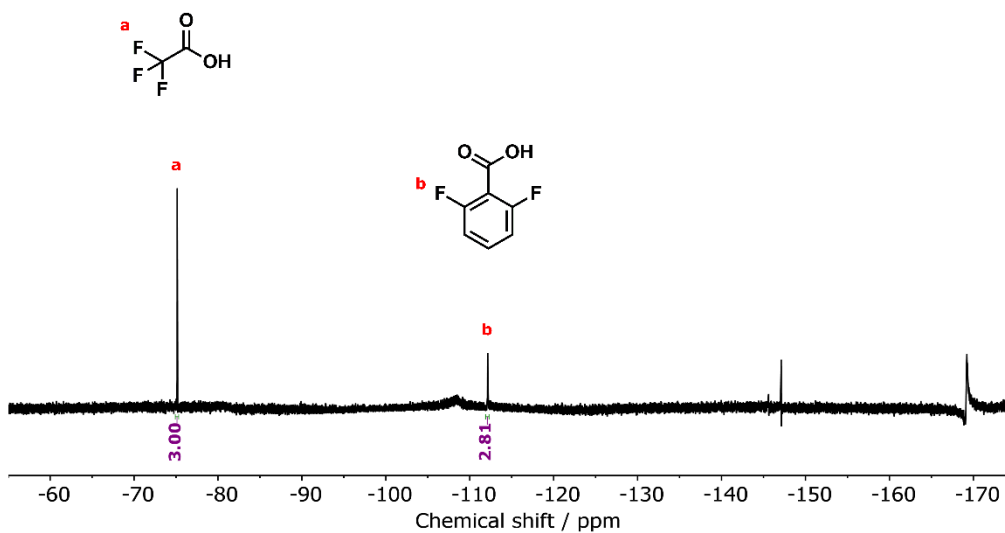


Figure S25. $^{19}\text{F-NMR}$ spectrum for Y-CU-45 washed with 0.1 M HCl for 2 days.

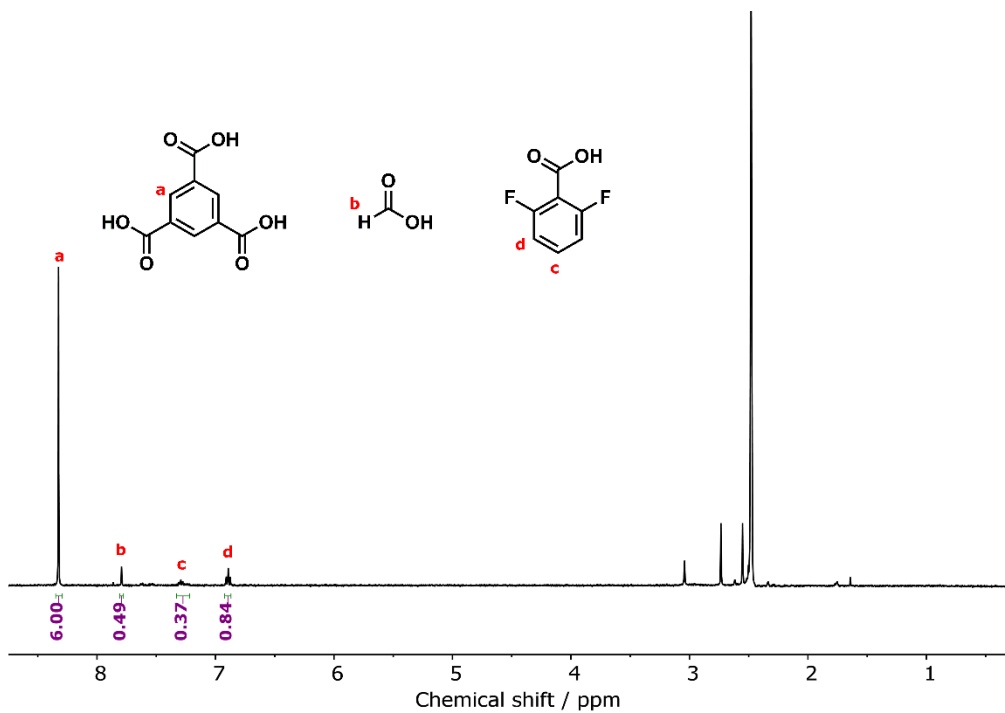


Figure S26. ¹H-NMR spectrum for Y-CU-45 washed with 0.1 M HCl for 3 days.

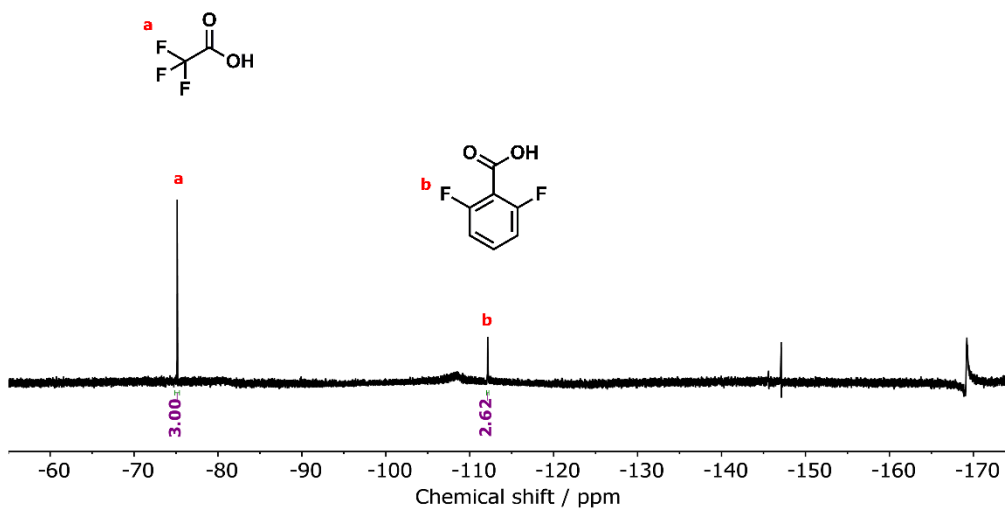


Figure S27. ¹⁹F-NMR spectrum for Y-CU-45 washed with 0.1 M HCl for 3 days.

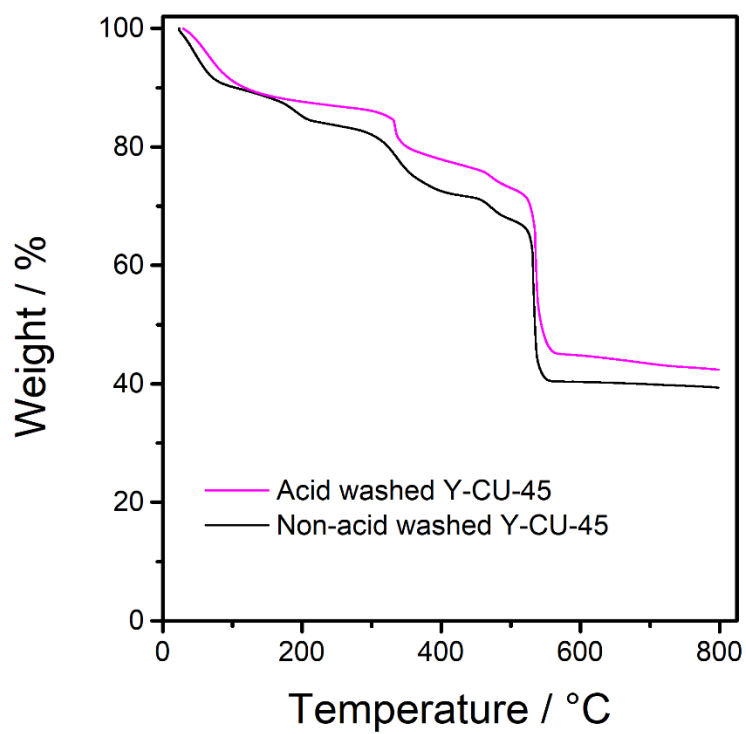


Figure S28. TGA curves of as-synthesized and acid washed Y-CU-45 samples performed under air.

Table S2. Crystal data and structure refinement parameters for Y-CU-45 at 100 K.

Temperature	100 K
Crystal color/habit	colourless/plate
Crystal size (mm)	(0.02 x 0.02 x 0.01)
Crystallizing solvent	DMF
Crystal system/ Space group	Cubic/ $Fd\bar{3}m$
a (Å)	36.079(4)
b (Å)	36.079(4)
c (Å)	36.079(4)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å ³)	46964(16)
Z/Z'	1/0.0052
Calculated density (g/cm ³)	0.850
F(000)	10454
Radiation	Synchrotron ($\lambda = 0.61990$ Å)
θ range (°)	1.633/22.618
Scan type	ϕ
Measured reflections	158966
Unique reflections	2242
Observed reflections	2004
$[F > 4\sigma(F)]$	
Final R (%)	3.95
wR2 (%)	13.13
Good-of-fit on $F^2(S)$	1.1280
$\Delta\rho$ max (e. Å ⁻³)	1.093
$\Delta\rho$ min (e. Å ⁻³)	-0.325
No of restraints/parameters	6/68
Data $[F > 4\sigma(F)]$ -to-parameter ratio	29.47

Table S3. Selected bond lengths and bond angles for Y-CU-45 at 100 K.

Bond lengths (Å)		Bond angles (°)			
Y1–O1	2.274(2)	O1–Y1–O2	128.77(9)	O2–Y1–F1	140.72(9)
Y1–O2	2.348(3)	O1–Y1–O3	70.1(2)	O2–Y1–F2	77.74(8)
Y1–O3	2.658(8)	O1–Y1–F1	78.21(7)	O3–Y1–F1	138.1(2)
Y1–F1	2.283(2)	O1–Y1–F2	139.44(7)	O3–Y1–F2	122.4(2)
Y1–F2	2.268(2)	O2–Y1–O3	58.8(2)	F1–Y1–F2	99.47(7)

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