Supporting Information for

Cerium-based Metal Organic Frameworks with UiO-66 Architecture: Synthesis, Properties and Redox Catalytic Activity

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1. Synthesis procedure

Materials and Methods. Cerium ammonium nitrate (98 %, $(NH_4)_2Ce(NO_3)_6$, Alfa Aesar), was used as purchased. Fumaric acid (99 %, H_2Fum, Aldrich), terephthalic acid (98 %, H_2BDC, Aldrich), 2-nitroterephthalic acid (98 %, $H_2BDC-NO_2$, Fluka), 2-methylterephthalonitrile (98 %, Aldrich), dimethyl-2-fluoroterephthalate (96 %, Aldrich), 2 chloro-1,4-dimethylbenzene (99 %, Aldrich), 1,2,4-benzenetricarboxylic acid (98 %, $H_2BDC-COOH$, TCI), dimethyl-2,6-naphthalenedicarboxylic acid (99 %, TCI) and 4,4' biphenyldicarboxylic acid dimethyl ester (99 %, Aldrich) were used without further purification.

The linker molecules 2-methylterephthalic acid ($H_2BDC-CH_3$), 2-fluoroterephthalic acid (H_2BDC-F), 2-chloroterephthalic acid ($H_2BDC-Cl$), 2,6-naphthalenedicarboxylic acid (H_2NDC) and 4,4'-biphenyldicarboxylic acid (H_2BPDC) were synthesized.

PXRD experiments for product identification were performed on a Stadi P Combi diffractometer with CuKα1 radiation equipped with an image-plate detector system and an xy-stage. The high resolution PXRD patterns were recorded on a Stadi P diffractometer using a Mythen detector. The PXRD measurement of activated Ce-UiO-66-BDC was carried out on a PANalytical Empyrean diffractometer equipped with a PIXcel3D detector and a hybrid monochromator using a sealed glass capillary. For temperature dependent X-ray diffraction measurements the PANalytical Empyrean diffractometer was equipped with a MRI TC radiation chamber with AlCr heater and Al_2O_3 crucibles. NMR spectra were measured on a Bruker DRX 500 spectrometer. Sorption experiments were performed using a BEL Japan Inc. Belsorpmax. The specific surface areas were determined using the Rouquerol approach and the micropore volume was calculated at $p/p0 = 0.5$. IR spectra were measured on a Bruker ALPHA-FT-IR A220/D-01 spectrometer equipped with an ATR unit. Thermogravimetric measurements were performed on a TA instruments Q500 under a flow of oxygen (10 ml min^{-1}) with a heating rate of 5 K min^{-1}.

Sample treatment prior to NMR measurements. Solution ^1H-NMR spectroscopy was carried out to establish the successful incorporation of linker molecules and to detect any linker modification. The products were dissolved in a mixture of 10 % deuterochloric acid (DCl) in D_2O and deuterated dimethyl sulfoxide (d_6-DMSO) (molar ratio 1:7) before ^1H-NMR spectra were recorded.

XANES spectra of Ce-UiO-66-BDC, $Ce(NO_3)_3$, $CeCl_3$ and $(NH_4)_2Ce(NO_3)_6$ were collected at I811 beamline of MAX II synchrotron in Lund, Sweden.[4] All the spectra were measured in transmission with a sampling step of 0.2 eV and an integration time of 1 s/point. Harmonic rejection was achieved detuning the Si(111) double crystal monochromator by 40%. The energy calibration was achieved using a Cr metal foil.

Catalytic experiments. Prior to reaction, Ce-UiO-66-BDC was evacuated overnight at 180 °C - 240 °C. Catalytic oxidation experiments were performed in stainless steel reactors equipped with a pressure gauge. Before reaction, 25 mg of evacuated Ce-UiO-66-BDC was weighed into the reactor under inert gas atmosphere. To this, a solution of benzyl alcohol (0.75 mmol), chlorobenzene (0.75 mmol; internal standard) and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO; 0.1125 - 0.225 mmol) in 8 ml acetonitrile was added. This results in a molar ratio of benzyl alcohol/Ce of 10. The reactor was subsequently flushed with O_2, and charged with 6 bar O_2 prior to reaction. The reaction proceeded under stirring at 110 °C for 7-24 h. Samples were analyzed using GC (Shimadzu GC 2010, CP-SIL-5 column). Nanoparticulate CeO_2 (Alfa Aesar, 15-30 nm) and Zr-UiO-66-BDC prepared by methods reported elsewhere[11] were also tested as reference materials. Samples were analyzed for benzoic acid formation using GC-MS (Agilent 6890 chromatograph, HP-5MS column, 5973 MSD detector) by silylating with an excess of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA; 2 h at 70 °C). The amount of Ce in solugiton was determined by ICP on a Perkin Elmer Optima 3300.

Synthesis of 2-methylterephthalic acid ($H_2BDC-CH_3$). 2 g (14.1 mmol) 2-methylterephthalonitrile was dissolved in 30 mL conc. sulphuric acid and heated at 90 °C for 24 h. After cooling to room temperature 15 mL demineralized water was added. The mixture was cooled to 0 °C and 2.72 g (39.4 mmol) sodium nitrite dissolved in 12 mL demin. water was added. After 24 h refluxing the mixture was cooled to room temperature, 80 mL demin. water was added, the precipitated solid filtered and washed with 50 mL demin. water. The colorless solid was dried in air at 50 °C. Yield: 2.31 g (12.8 mmol, 91%).

^1H-NMR (500 MHz, 300 K, DMSO-d_6): δ = 13.15 (s, 2 H, COOH), 7.88 (d, 1 H), 7.85 (d, 1 H), 7.81 (dd, 1 H), 2.55 (s, 3 H, CH_3) ppm.

Synthesis of 2-fluoroterephthalic acid (H_2BDC-F). 0.5 g (2.36 mmol) dimethyl-2-fluoroterephthalate and 1.98 g (47.1 mmol) lithium hydroxide monohydrate were dissolved in a mixture of 50 mL tetrahydrofuran and 50 mL water. The mixture was stirred 30 min at an elevated temperature (80 °C) and afterwards 24 h at room temperature. The liquid was brought to pH~1 by adding concentrated hydrochloric acid and the amount of solvent was reduced under reduced pressure. The precipitated solid was filtered, washed with 50 mL demin. water and dried in air at 50 °C. Yield: 358 mg (1.97 mmol, 90%).

^1H-NMR (500 MHz, 300 K, DMSO-d_6): δ = 13.56 (s, 2 H, COOH), 7.96 (dd, 1 H), 7.82 (dd, 1 H), 7.73 (dd, 1 H) ppm.

^{19}F-NMR (470.6 MHz, 300 K, DMSO-d_6): δ = -110.23 (dd, 1 F) ppm.

Synthesis of 2-chloroterephthalic acid (H_2BDC-Cl). 3.17 g (22.5 mmol) 2-chloro-1,4-dimethylbenzene and 16 ml nitric acid (70%) were mixed with 30 ml demineralized water. The mixture was placed in a 125 ml Teflon-lined steel autoclaved and heated at 170°C for 16 hours. The precipitated solid was filtered, washed with 500 ml demineralized water and dried under vacuum at 70 °C. Yield: 3.78 g (18.9 mmol, 84%).

^{1}H-NMR (500 MHz, 300 K, NaOD (5%) / D_2O): δ = 7.66 (d, 1 H), 7.56 (dd, 1 H), 7.23 (d, 1 H) ppm.

Synthesis of 2,6-naphthalenedicarboxylic acid (H_2NDC). 20 g (81.8 mmol) dimethyl-2,6-naphthalenedicarboxylic acid and 8.36 g (209 mmol) sodiumhydroxide were dissolved in 200 mL water. After 12 h refluxing the mixture was cooled to room temperature and 1000 mL demin. water was added. The liquid was brought to pH~1 by adding concentrated hydrochloric acid, the precipitated solid was filtered, washed with 500 mL demin. water and dried in air at 70 °C. Yield: 16.34 g (75.6 mmol, 92%).

^{1}H-NMR (200 MHz, 300 K, DMSO-d_6): δ = 13.24 (s, 2 H, COOH), 8.66 (d, 2 H), 8.21 (d, 2 H), 8.04 (dd, 2 H) ppm.

Synthesis of 4,4'-biphenyldicarboxylic acid (H_2BPDC). 9 g (37.0 mmol) 4,4'-biphenyldicarboxylic acid, dimethyl ester and 3.76 g (94 mmol) sodiumhydroxide were dissolved in a mixture of 100 mL tetrahydrofuran and 100 mL water. The mixture was stirred 24 h at an elevated temperature (80 °C). After 24 h refluxing the mixture was cooled to room temperature and brought to pH~1 by adding concentrated hydrochloric acid. The amount of solvent was reduced under reduced pressure and the precipitated solid was filtered, washed with 100 mL water and dried in air at 70 °C. Yield: 7.92 g (32.7 mmol, 88%).

^{1}H-NMR (200 MHz, 300 K, DMSO): δ = 8.05 (d, 2 H), 7.86 (d, 2 H) ppm.

Synthesis of Ce-UiO-66-BDC. All products were synthesized using Pyrex glass reaction tubes (maximum volume 8 mL). 1,4-benzendicarboxylic acid (H_2BDC, 35.4 mg, 213 μmol) was introduced into the glass reactor. After the addition of N,N-dimethylformamide (DMF; 1.2 mL) an aqueous solution of cerium(IV) ammonium nitrate (400 μL, 0.5333 M) was added. The glass reactor was sealed and heated using an aluminum heater block under stirring for 15 min at 100 °C. The light yellow precipitate was centrifuged in the mother liquor, which was then decanted off, before being re-dispersed and centrifuged twice in DMF (2 mL). To remove DMF from the product, the solid was washed and centrifuged with acetone (2 mL) four times. The resulting white solid was dried in air at 70 °C.

This synthesis procedure has also been successfully scaled up in larger glass reactor vessels with volumes up to 12.8 mL and in Teflon-lined microwave autoclaves using 32 ml of synthesis mixture.

PXRD measurements demonstrate that at reaction times longer than 2 h the cerium formate[3] $Ce(HCOO)_3$ is formed.

Synthesis of Ce-UiO-66-Fum, -NDC, -BPDC and Ce-UiO-66-BDC-X functionalized derivatives. An amount of linker equivalent to 213 µmol was placed in a glass reaction tube. Then DMF (1.2 ml) was added followed by an aqueous solution of cerium ammonium nitrate (400 µL, 0.5333 M). The glass reactor was sealed and heated using an aluminum heating block under stirring for 15 min at 100 °C. After the reaction, Ce-UiO-66-Fum and Ce-UiO-66-BDC-X were purified following the washing procedure described for Ce-UiO-66-BDC. For Ce-UiO-66-NDC and -BPDC it was necessary to remove unreacted linker molecules by washing and centrifuging with DMSO (2 × 2 mL) first. This step was followed by solvent exchange and centrifugation with DMF (4 × 2 mL). The resulting solids were dried in air at room temperature.

2. Characterization by scanning electron microscopy and powder X-ray diffraction

All compounds were obtained as microcrystalline powders. Structures were confirmed from PXRD data. The structures of Ce-UiO-66-BDC and Ce-UiO-66-Fum were determined by Rietveld refinement (Figure S1-2) using TOPAS-Academic v5,[1] with initial structures developed by model building using Materials Studio v4.3.[2] For Ce-UiO-66-Fum, oxygen atoms of water molecules were located by repeated cycles of Fourier difference mapping followed by simulated annealing and Rietveld refinement. Attempts to model the positions of the DMF molecules in the pores of Ce-UiO-66-NDC and -BPDC were unsuccessful and thus only the unit cells of these compounds were determined by Le Bail profile fitting using TOPAS-Academic v5 (Figure S6-7). Crystallographic details for all four compounds are given in Table S1. For the functionalized Ce-UiO-66-BDC-X derivatives Le Bail profile fitting was used to obtain the lattice parameters (Table S2, Figures S9-13).

Table S1. Crystallographic data of the compounds Ce-UiO-66-BDC, -Fum, -NDC and -BPDC.

	Ce-UiO-66-Fum	**Ce-UiO-66-BDC**	**Ce-UiO-66-NDC**	**Ce-UiO-66-BPDC**
Formula Sum	$C_{24}H_{16}O_{32}Ce_6$	$C_{48}H_{28}O_{32}Ce_6$	$C_{72}H_{40}O_{32}Ce_6$	$C_{84}H_{52}O_{32}Ce_6$
Wavelength /Å	CuKα_1	CuKα_1	CuKα_1	CuKα_1
a /Å	18.5728(2)	21.4727(3)	24.6240 (1)	27.5836 (2)
Volume /Å^3	6406.4(2)	9900.6(4)	14930.5(2)	20987.1(4)
Spacegroup	$Pn\bar{3}$	$Fm\bar{3}m$	$Fm\bar{3}m$	$Fm\bar{3}m$
R_{wp} / %	5.05	2.65	4.85	5.12
R_{Bragg} / %	1.62	5.86	-	-
GoF	1.180	2.268	1.108	1.374
Number of Atoms	16	6	-	-
Number of Restraints	23	18	-	-
Number of Parameters	72	69	-	-

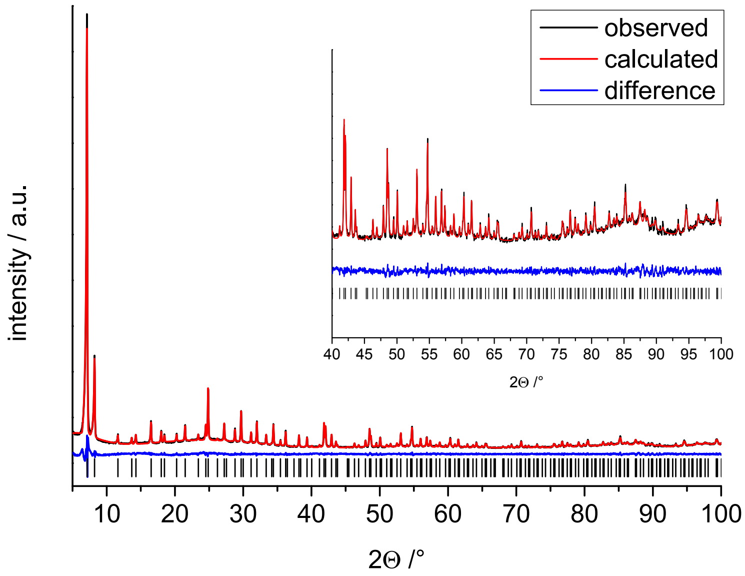

Figure S1	Final Rietveld plot of Ce-UiO-66-BDC. The observed PXRD pattern is shown in black, the calculated one is red and the difference (observed – calculated) of both patterns is given by the blue line. The allowed positions of the Bragg peaks are given by as black ticks.

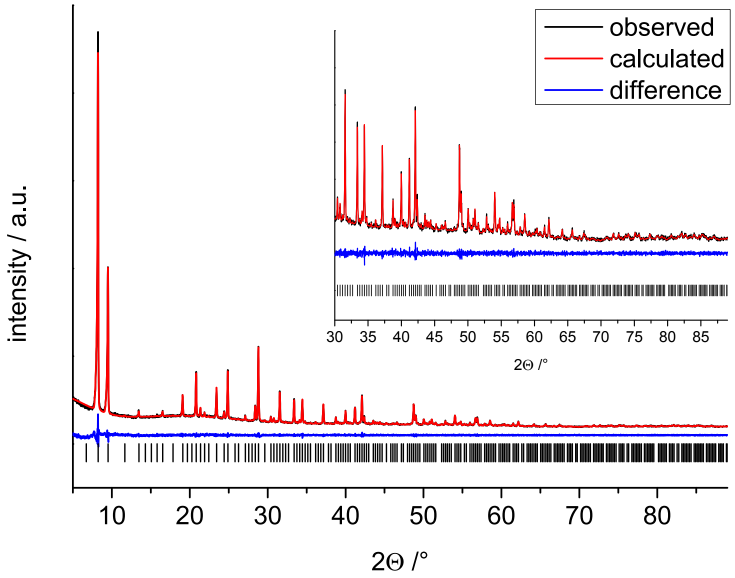

Figure S2	Final Rietveld plot of Ce-UiO-66-Fum. The observed PXRD pattern is shown in black, the calculated one is red and the difference (observed – calculated) of both pattern is given by the blue line. The allowed positions of the Bragg peaks are given by as black tics.

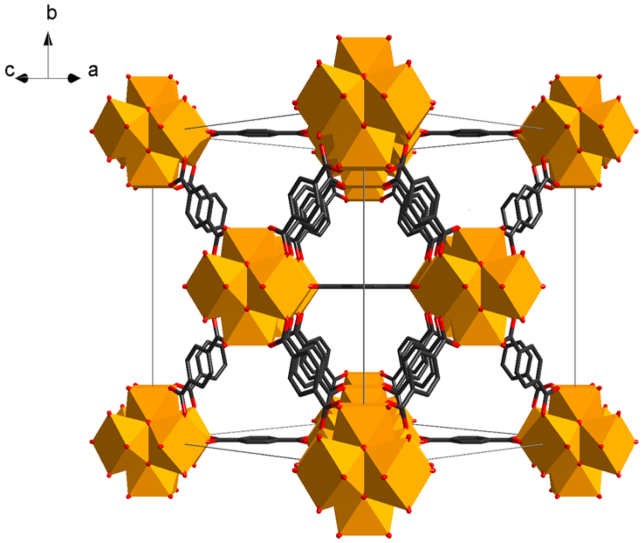

Figure S3 Unit cell of compound Ce-UiO-66-BDC. The structure is constructed of $[Ce_6O_4(OH)_4]^{12+}$ clusters that are 12-fold connected through terephthalate, resulting in a highly packed fcc structure with tetrahedral and octahedral cages.

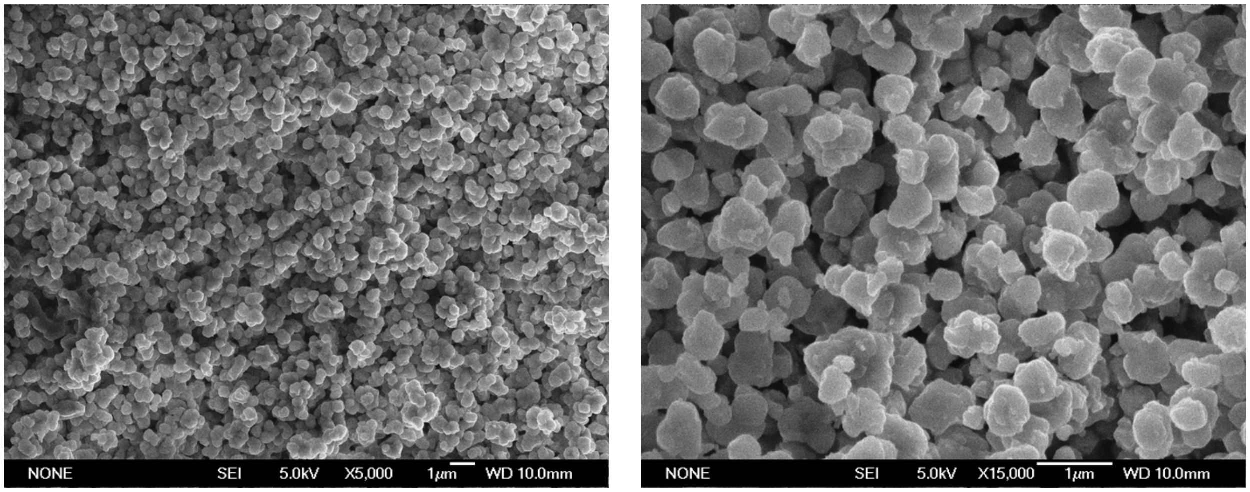

Figure S4 SEM images of Ce-UiO-66-BDC.

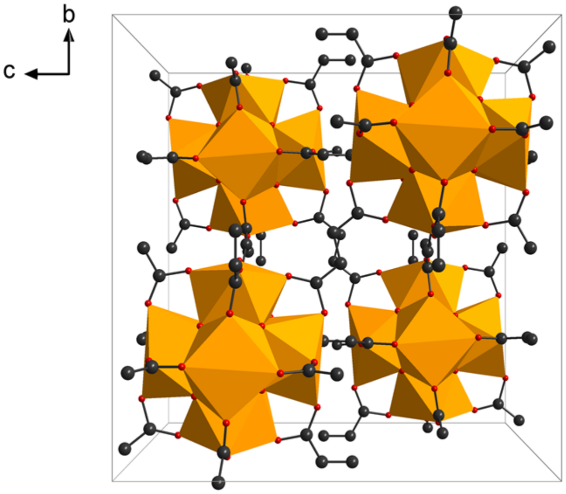

Figure S5 The unit cell of compound Ce-UiO-66-Fum contains four $[Ce_6O_4(OH)_4]^{12+}$ clusters arranged in a tetrahedral configuration that are 12-fold connected through fumarate linkers.

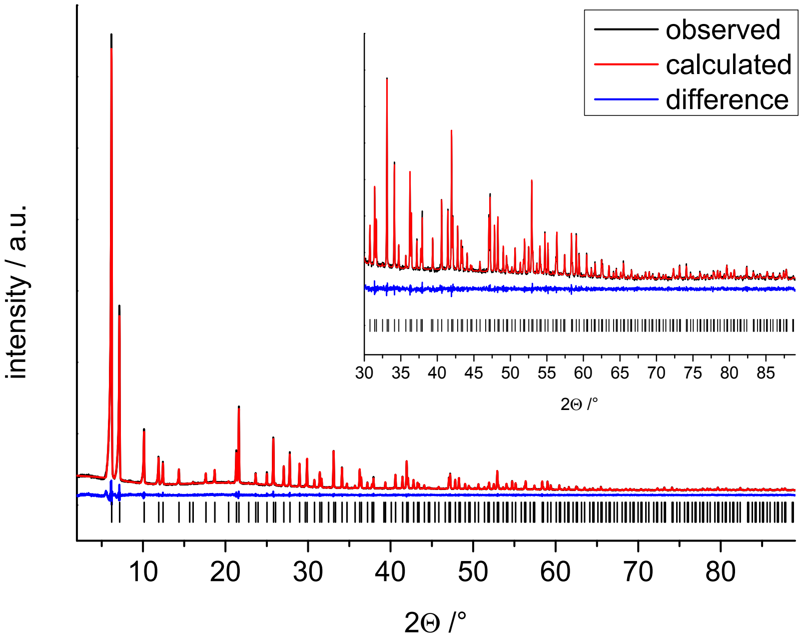

Figure S6 Le Bail plot of Ce-UiO-66-NDC. The observed PXRD pattern is shown in black, the calculated one is red and the difference (observed – calculated) of both pattern is given by the blue line. The allowed positions of the Bragg peaks are given by as black tics.

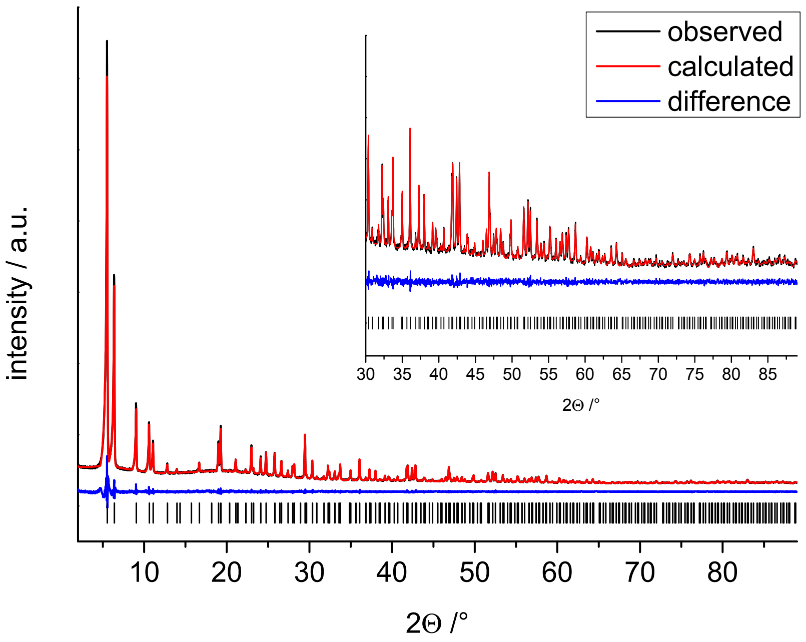

Figure S7 Le Bail plot of Ce-UiO-66-BPDC. The observed PXRD pattern is shown in black, the calculated one is red and the difference (observed – calculated) of both pattern is given by the blue line. The allowed positions of the Bragg peaks are given by as black tics.

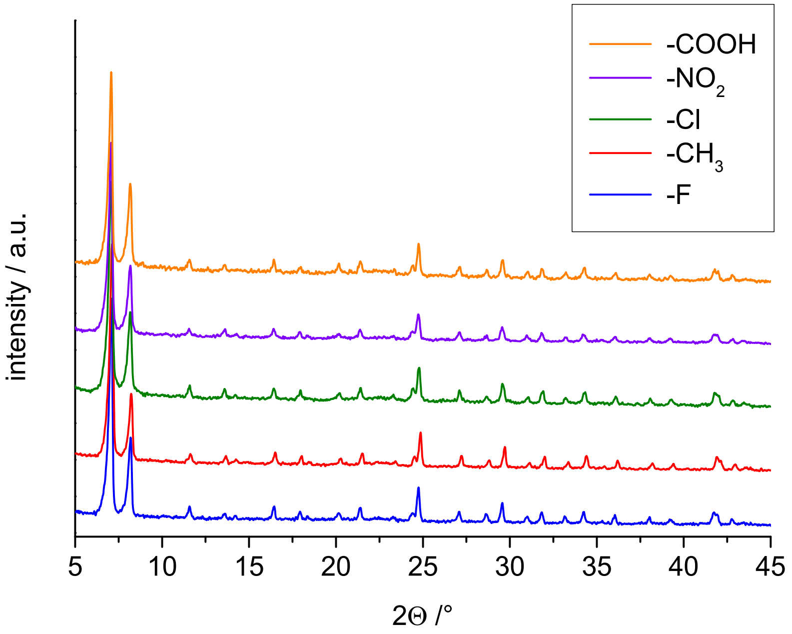

Figure S8 PXRD patterns of functionalized Ce-UiO-66-BDC-X (X= F, CH_3, Cl, NO_2, COOH) derivatives.

Table S2 Lattice parameters of functionalized Ce-UiO-66-BDC-X as obtained from Le Bail fits (Figure S6-S10).

Compound	*a* [Å]	*α* [°]	spacegroup	R_{wp}	GoF
Ce-UiO-66-BDC-F	21.5241(8)	90	$Fm\bar{3}m$	7.47	1.35
Ce-UiO-66-BDC-CH_3	21.4842(2)	90	$Fm\bar{3}m$	5.31	1.43
Ce-UiO-66-BDC-Cl	21.4904(2)	90	$Fm\bar{3}m$	5.55	1.12
Ce-UiO-66-BDC-NO_2	21.5194(2)	90	$Fm\bar{3}m$	5.74	1.13
Ce-UiO-66-BDC-COOH	21.4718(7)	90	$Fm\bar{3}m$	6.89	1.22

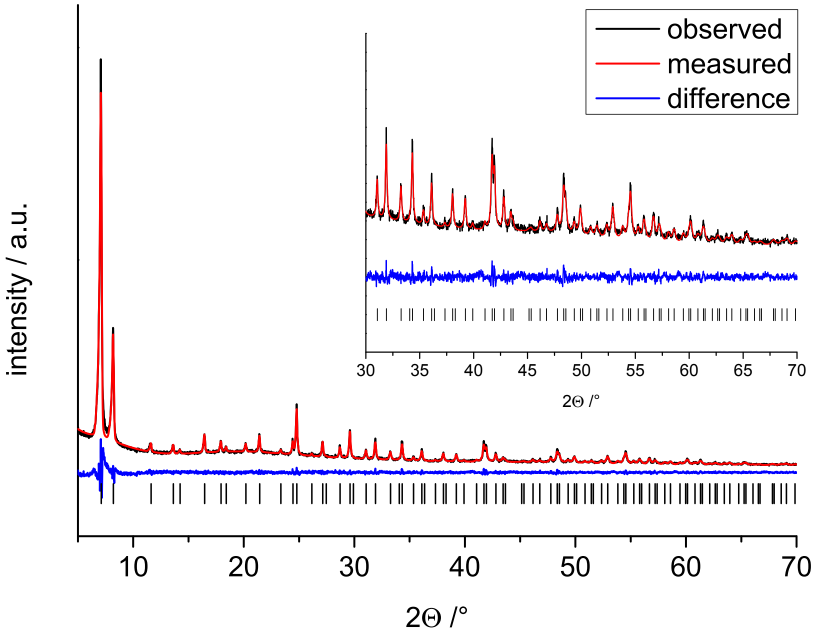

Figure S9 Le Bail plot of Ce-UiO-66-BDC-F.

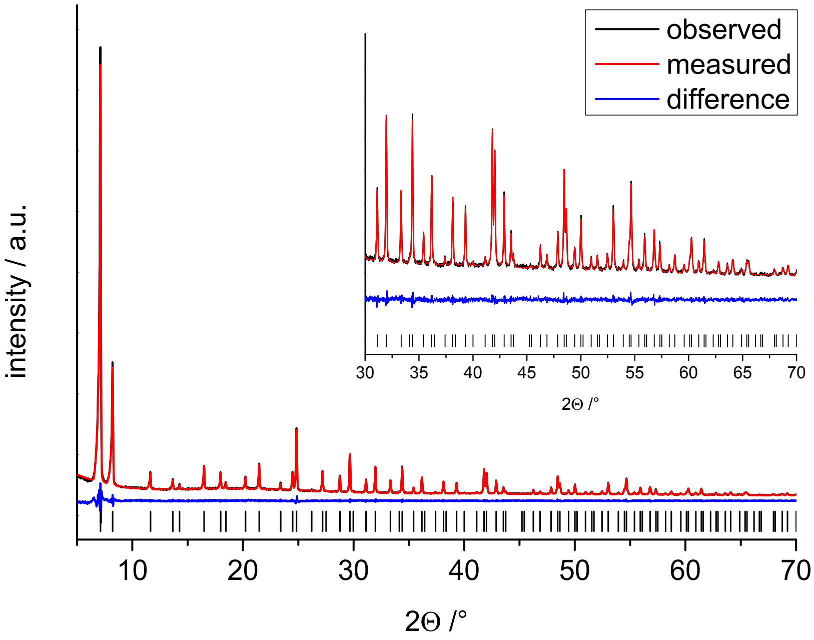

Figure S10 Le Bail plot of Ce-UiO-66-BDC-CH_3.

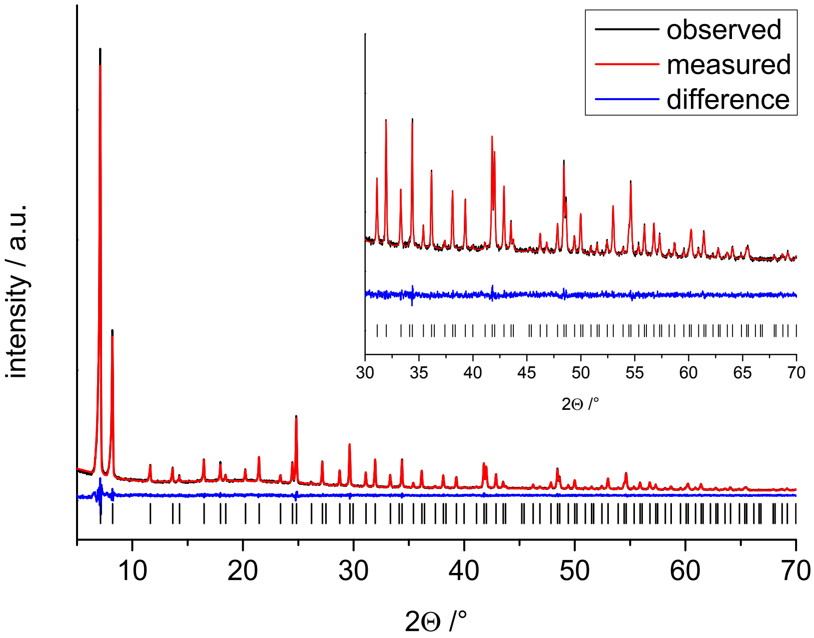

Figure S11 Le Bail plot of Ce-UiO-66-BDC-Cl.

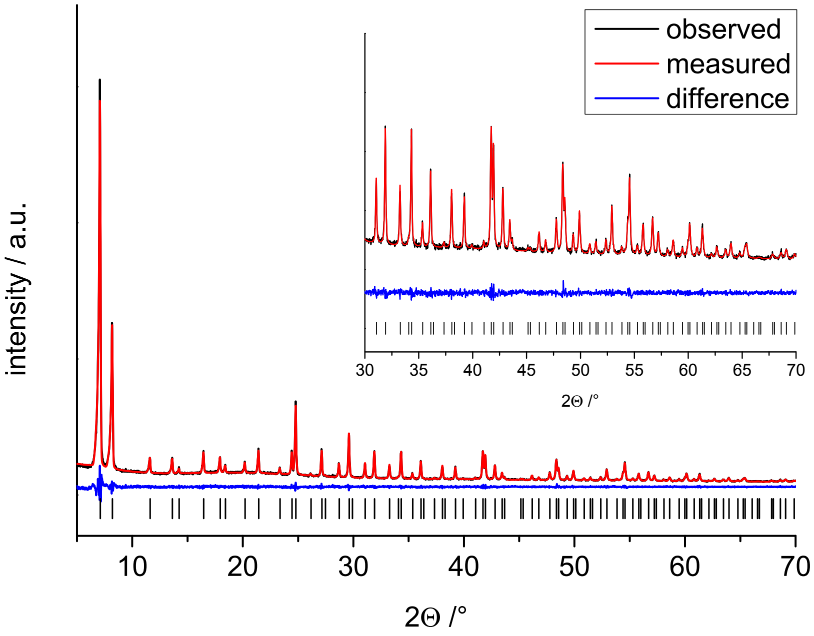

Figure S12 Le Bail plot of Ce-UiO-66-BDC-NO_2.

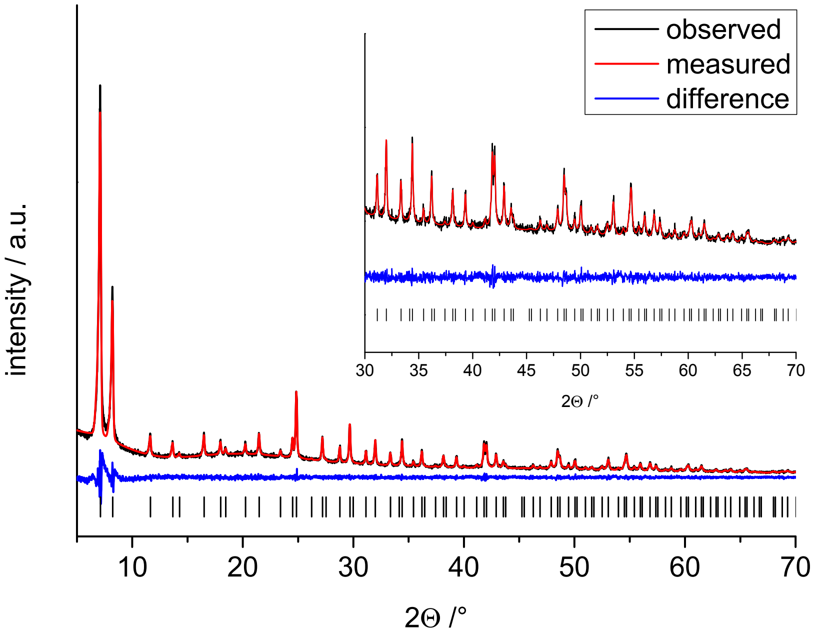

Figure S13 Le Bail plot of Ce-UiO-66-BDC-COOH.

3. Chemical and thermal analysis

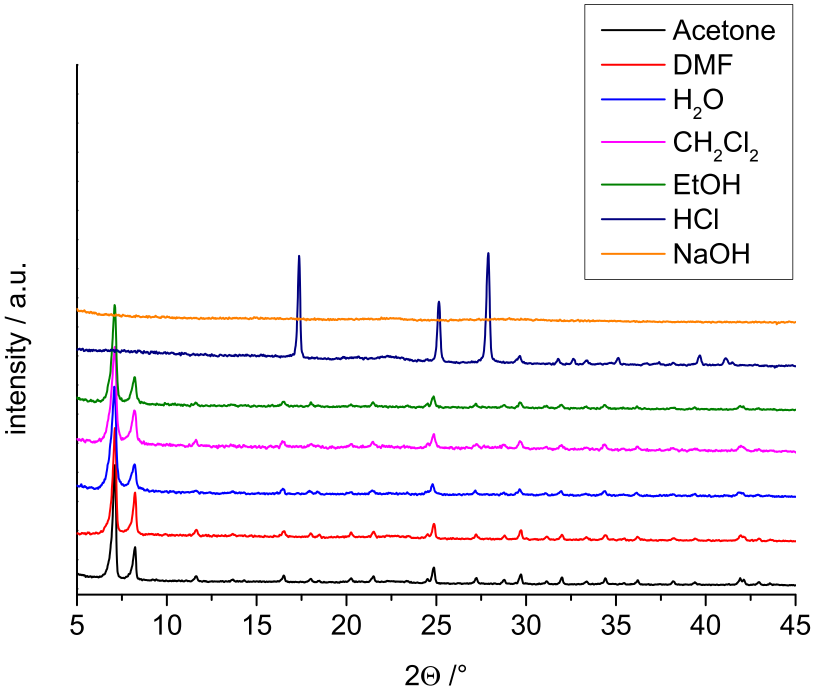

Figure S14 PXRD pattern of Ce-UiO-66-BDC after stirring in different solvents for 24 h at room temperature. The product after treating with 2 M HCl solution is H_2BDC.

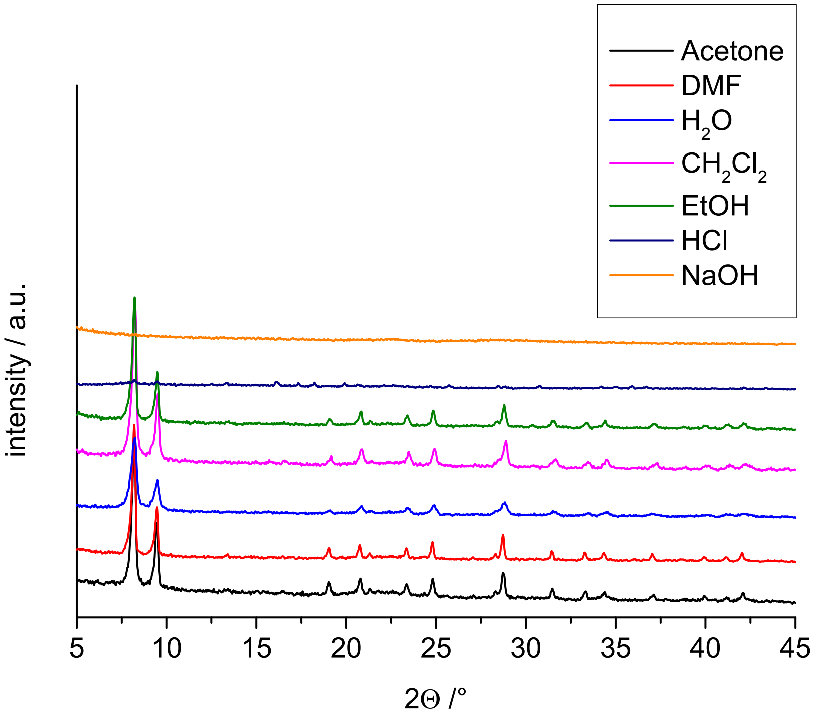

Figure S15 Powder pattern of Ce-UiO-66-Fum after stirring in different solvents.

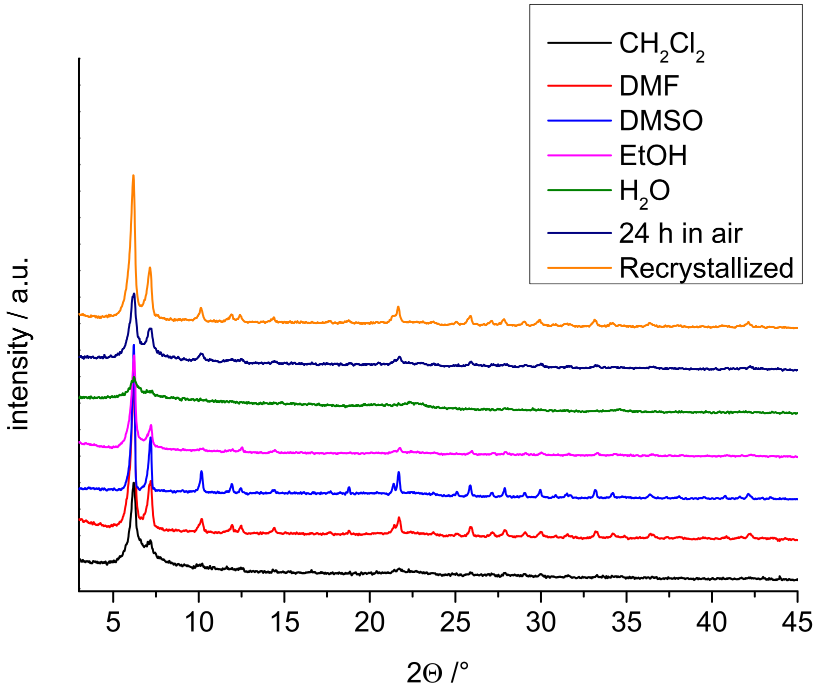

Figure S16 Powder pattern of Ce-UiO-66-NDC after stirring in different solvents.

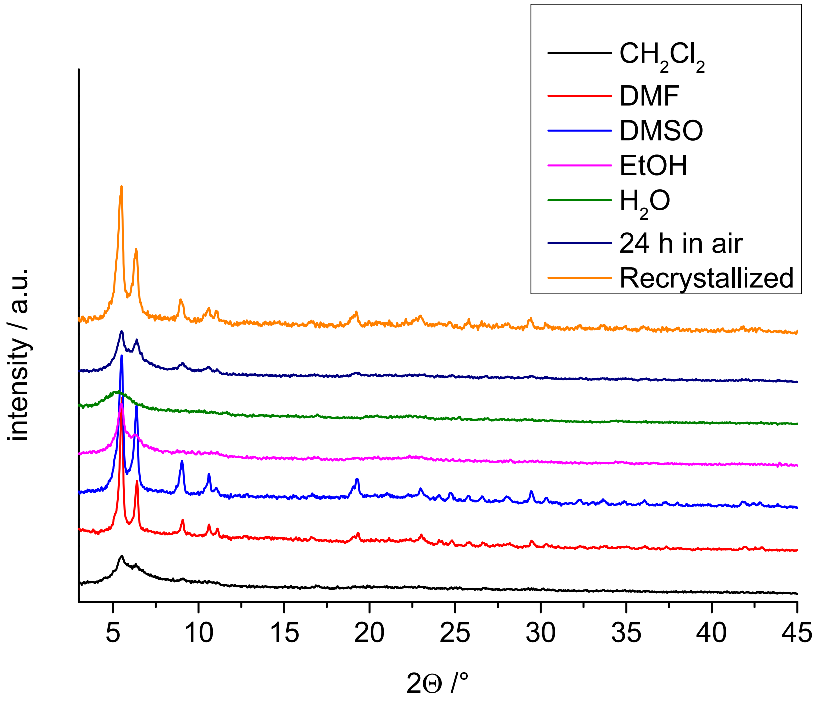

Figure S17 Powder pattern of Ce-UiO-66-BPDC after stirring in different solvents.

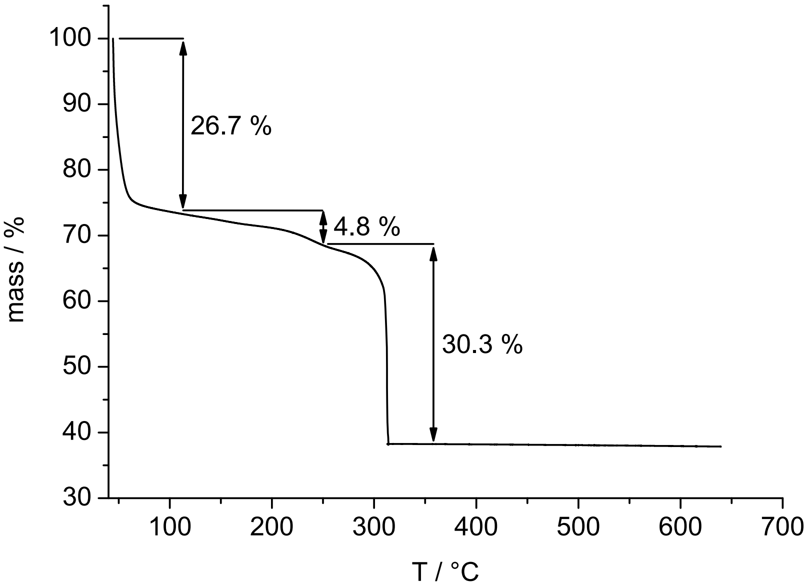

Figure S18 TG curve of Ce-UiO-66-BDC in an oxygen atmosphere.

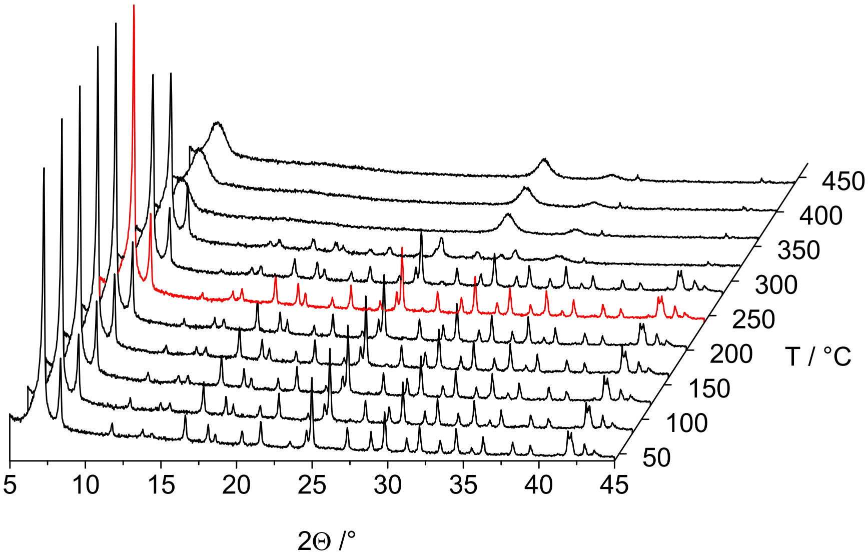

Figure S19 Results of the temperature dependent PXRD measurement of Ce-UiO-66-BDC. The red PXRD pattern marks the temperature (240 °C) to which the compound is stable.

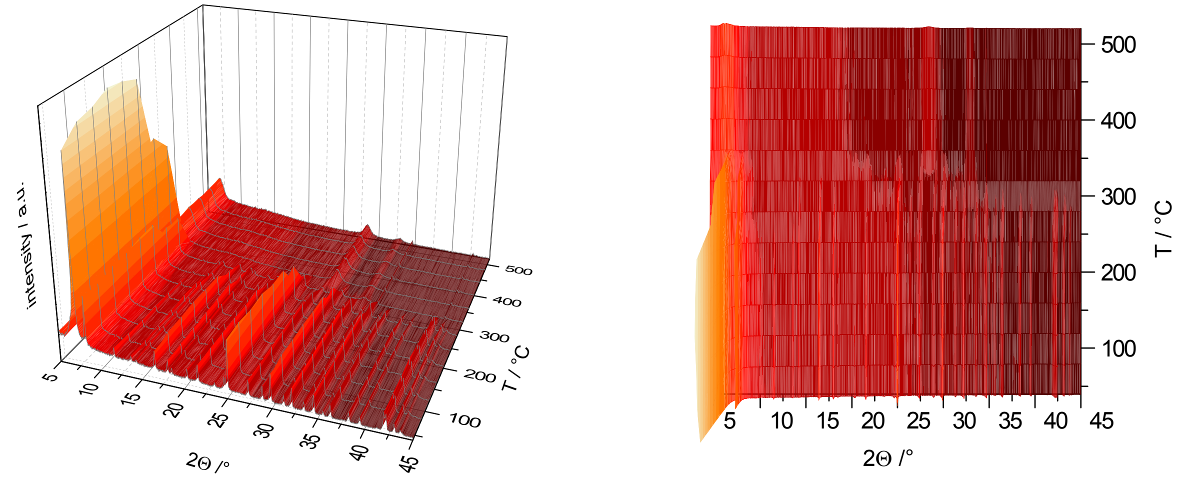

Figure S20 Results of the temperature dependent PXRD measurement of Ce-UiO-66-BDC (left) and top view (right).

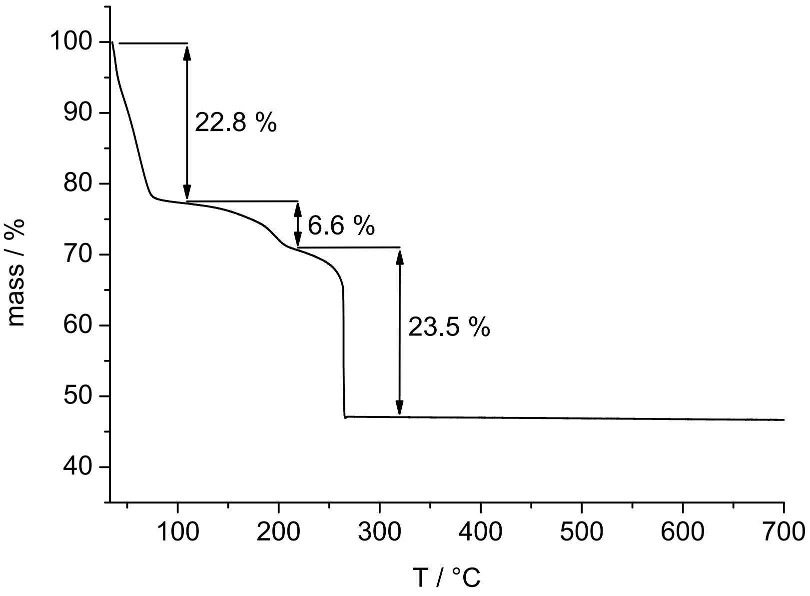

Figure S21 TG curve of Ce-UiO-66-Fum heated in oxygen atmosphere. The first two steps, 22.8 wt.% (25-100°C) and 6.6 wt.% (100-160°C) are assigned to the loss of physisorbed acetone and residues of DMF molecules respectively. Decomposition of the framework occurs at 220°C and again the weight loss indicates that on average each cluster is coordinated by 11 fumarate ligands rather than 12.

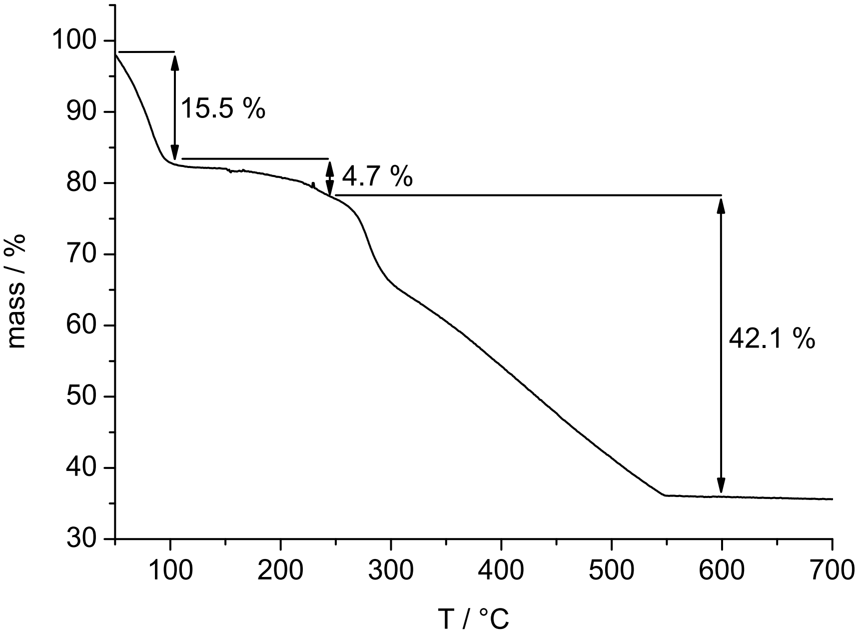

Figure S22 TG curve of Ce-UiO-66-BDC-NO_2 in air.

4. IR spectroscopy

The anti-symmetric (1590-1550 cm^{-1}) and symmetric (1390-1370 cm^{-1}) stretches of the carboxylate groups are present in the spectra of all four compounds, respectively. Adsorption bands due to the adsorbed solvents are also observed: C=O stretch of acetone in Ce-UiO-66-BDC and –Fum (1670 cm^{-1}); and C-H (2930 cm^{-1}) and C=O (1650 cm^{-1}) stretches of adsorbed DMF molecules in Ce-UiO-66-NDC and –BPDC.

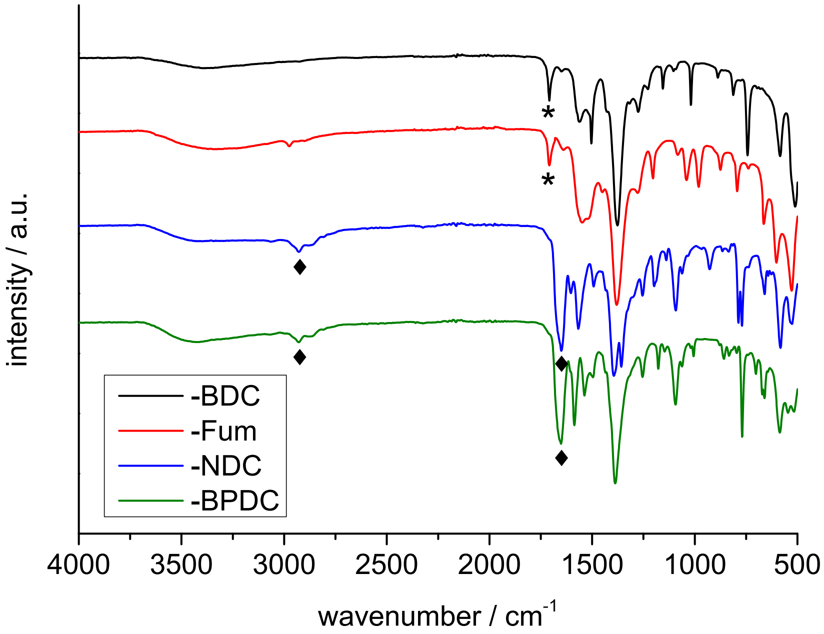

Figure S23 IR spectra of acetone exchanged Ce-UiO-66-BDC, and –Fum as well as DMF treated Ce-UiO-66-NDC and -BPDC. Bands of adsorbed acetone (stars) and DMF (diamonds) are marked in the spectra.

For the Ce-UiO-66-BDC-X compounds, IR spectroscopy the presence of the various functional groups can be confirmed from their characteristic bands. The halogenated compounds Ce-UiO-66-BDC-F and -Cl show the C-F and C-Cl stretching vibrations at 1225 cm^{-1} and 1050 cm^{-1} respectively. The methyl-functionalized compound shows very weak C-H stretching modes (2971-2926 cm^{-1}) and a vibration associated with the deformation of the methyl group (1398 cm^{-1}). For the $–NO_2$ functionalised material, the anti-symmetric stretch (1534 cm^{-1}) was observed;

and the carbonyl vibration of the uncoordinated –COOH functionalised compound (1697 cm^{-1}) could also be identified.

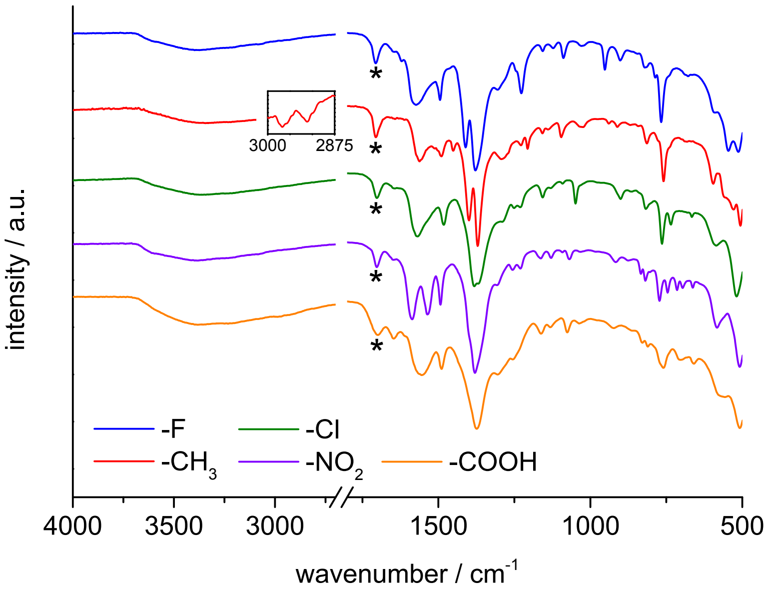

Figure S24 IR spectra of functionalized Ce-UiO-66-BDC-X derivatives with X= -F, -CH$_3$, -Cl, -NO$_2$, -COOH. The C=O stretching vibration of acetone is marked with stars. For Ce-UiO-66-BDC-CH$_3$ the area of the C-H stretching modes (3000-2875 cm^{-1}) is enlarged.

5. NMR spectroscopy

The products were dissolved in a mixture of 10 % deuterochloric acid (DCl) in D_2O and deuterated dimethyl sulphoxide (d_6-DMSO) (molar ratio 1:7) before ^{1}H-NMR spectra were recorded. In addition to the signals of DMSO (2.5 ppm) and D_2O (3.5-4.5 ppm) also acetone (2.08 ppm) can be identified, which was originally adsorbed into the framework.

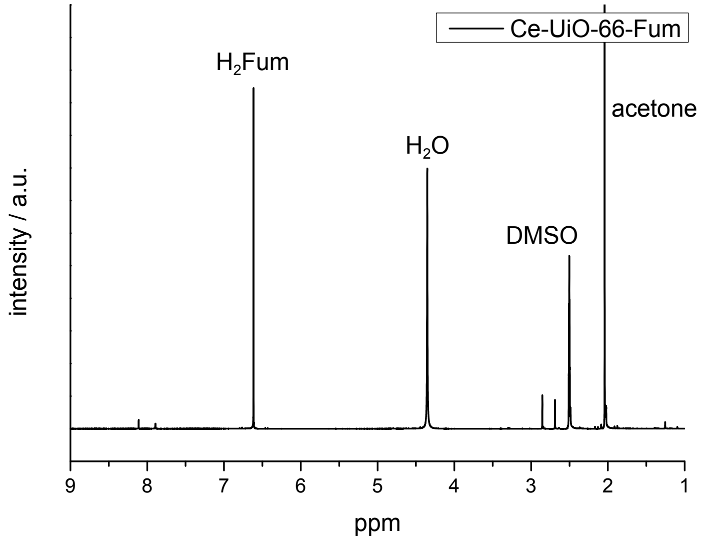

Figure S25 ^{1}H-NMR spectrum of dissolved Ce-UiO-66-Fum. ^{1}H-NMR (500 MHz, 300 K, DMSO-d_6): $\delta = 6.62$ (s, 2 H, H_2Fum) ppm.

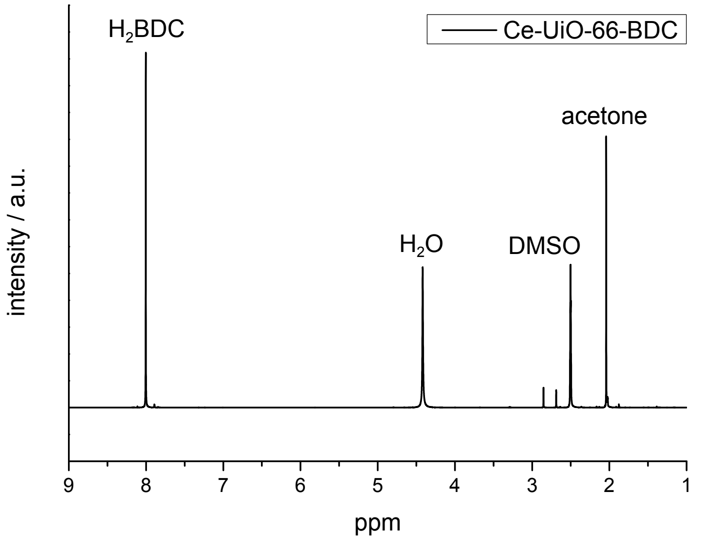

Figure S26 ^{1}H-NMR spectrum of dissolved Ce-UiO-66-BDC. ^{1}H-NMR (500 MHz, 300 K, DMSO-d$_6$): $\delta = 8.00$ (s, 4 H, H$_2$BDC) ppm.

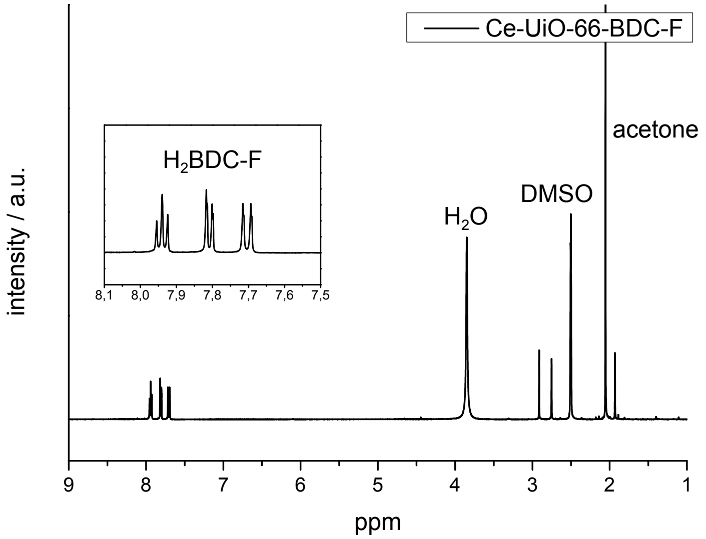

Figure S27 ^{1}H-NMR spectrum of dissolved Ce-UiO-66-BDC-F. ^{1}H-NMR (500 MHz, 300 K, DMSO-d$_6$): $\delta = 7.94$ (dd, 1 H, H$_2$BDC-F), 7.81 (dd, 1 H, H$_2$BDC-F), 7.70 (dd, 1 H, H$_2$BDC-F) ppm.

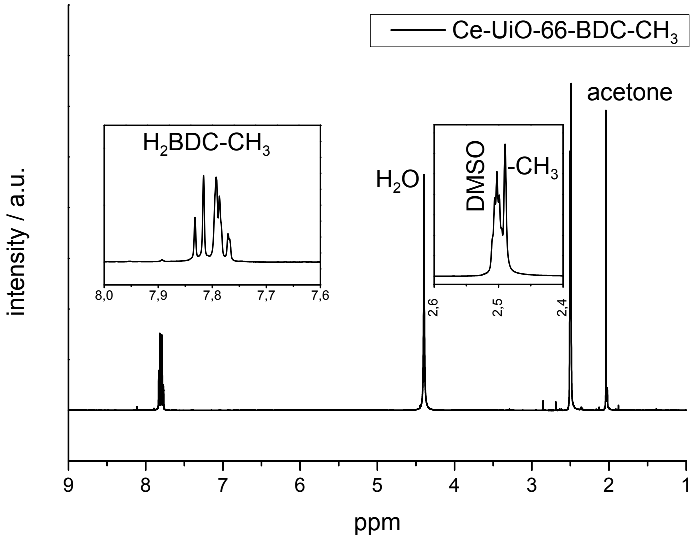

Figure S28 ^{1}H-NMR spectrum of dissolved Ce-UiO-66-BDC-CH$_3$. ^{1}H-NMR (500 MHz, 300 K, DMSO-d$_6$): δ = 7.82 (d, 1 H, H_2BDC-CH$_3$), 7.79-7.76 (m, 2 H, H_2BDC-CH$_3$), 2.49 (s, 3 H, CH$_3$) ppm.

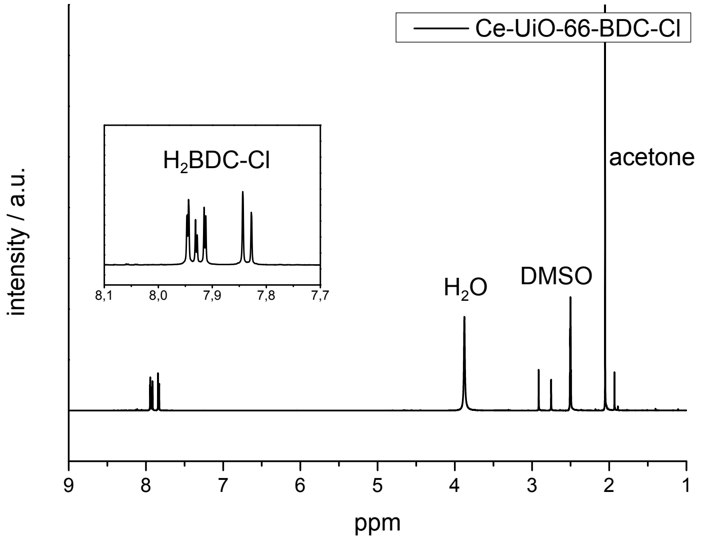

Figure S29 ^{1}H-NMR spectrum of dissolved Ce-UiO-66-BDC-Cl. ^{1}H-NMR (500 MHz, 300 K, DMSO-d$_6$): δ = 7.95 (d, 1 H, H_2BDC-Cl), 7.92 (d, 1 H, H_2BDC-Cl), 7.83 (d, 1 H, H_2BDC-Cl) ppm.

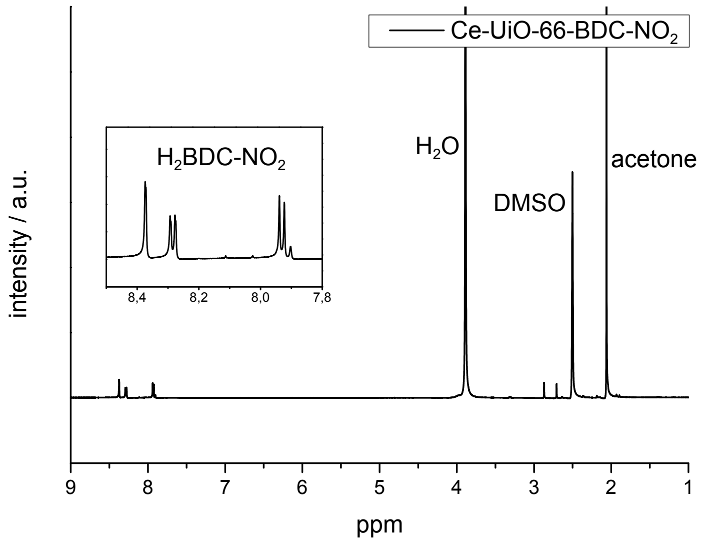

Figure S30 ^{1}H-NMR spectrum of dissolved Ce-UiO-66-BDC-NO$_2$. ^{1}H-NMR (500 MHz, 300 K, DMSO-d$_6$): δ = 8.37 (d, 1 H, H$_2$BDC-NO$_2$), 8.28 (dd, 1 H, H$_2$BDC-NO$_2$), 7.93 (d, 1 H, H$_2$BDC-NO$_2$) ppm.

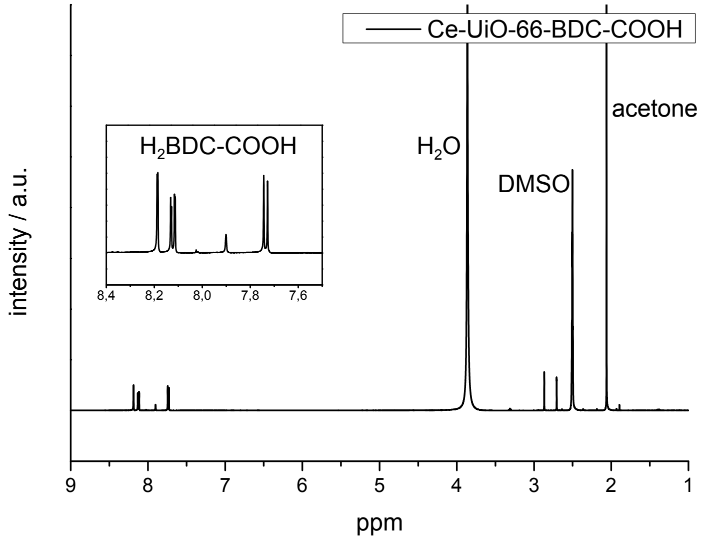

Figure S31 ^{1}H-NMR spectrum of dissolved Ce-UiO-66-BDC-COOH. ^{1}H-NMR (500 MHz, 300 K, DMSO-d$_6$): δ = 8.18 (d, 1 H, H$_2$BDC-COOH), 8.12 (dd, 1 H, H$_2$BDC-COOH), 7.73 (d, 1 H, H$_2$BDC-COOH) ppm.

N_2 sorption measurements

Prior to the sorption measurements the samples were activated at 100 °C and 10^{-2} kPa. An exception is the activation of Ce-UiO-66-BDC which exhibits a higher thermal stability and was therefore activated at 130 °C and 10^{-2} kPa.

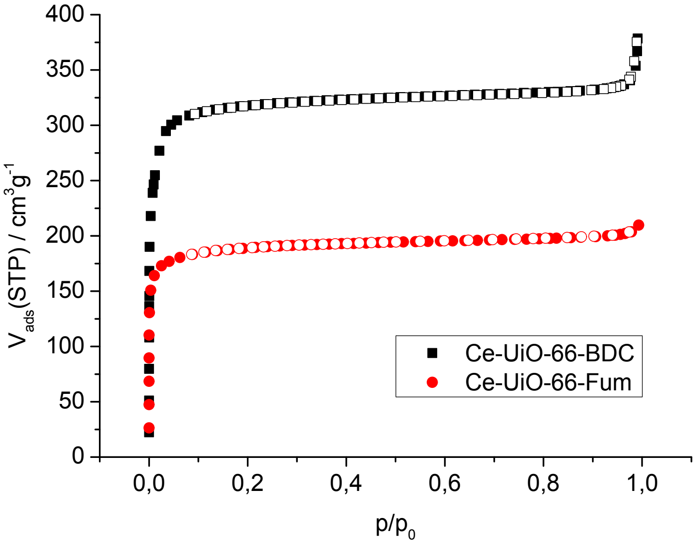

Figure S32 Results of nitrogen sorption measurements of Ce-UiO-66-BDC and Ce-UiO-66-Fum. Filled symbols mark the adsorption, while empty symbols mark the desorption step.

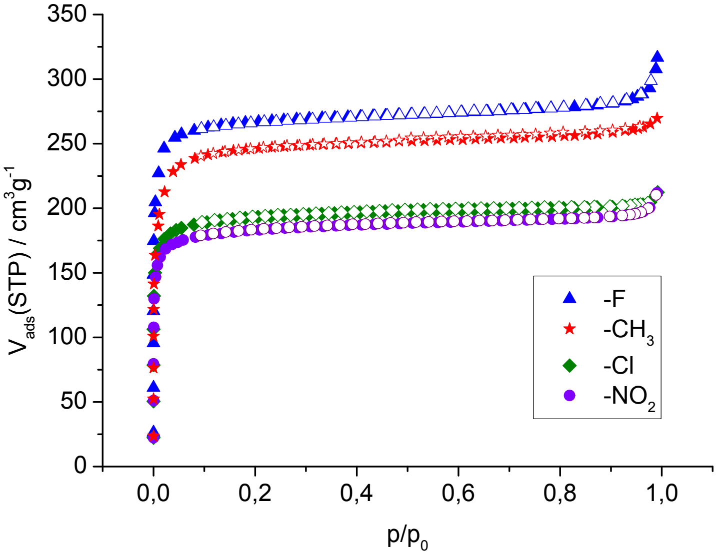

Figure S33 Results of nitrogen sorption measurements of functionalized Ce-UiO-66-BDC-X derivatives. Filled symbols mark the adsorption, while empty symbols mark the desorption step.

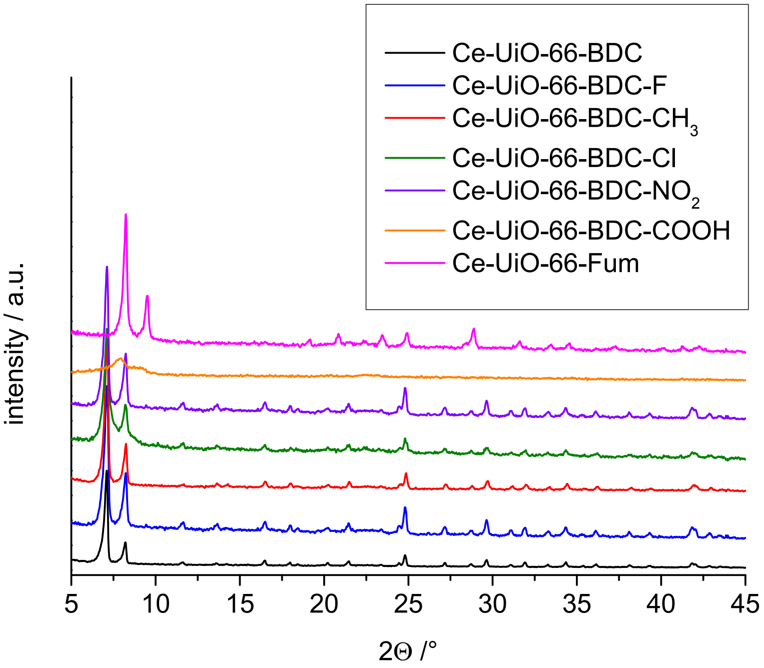

Figure S34 PXRD patterns of Ce-UiO-66-Fum, Ce-UiO-66-BDC and functionalized Ce-UiO-66-BDC-X derivatives after N_2 sorption measurement.

6. Catalytic studies

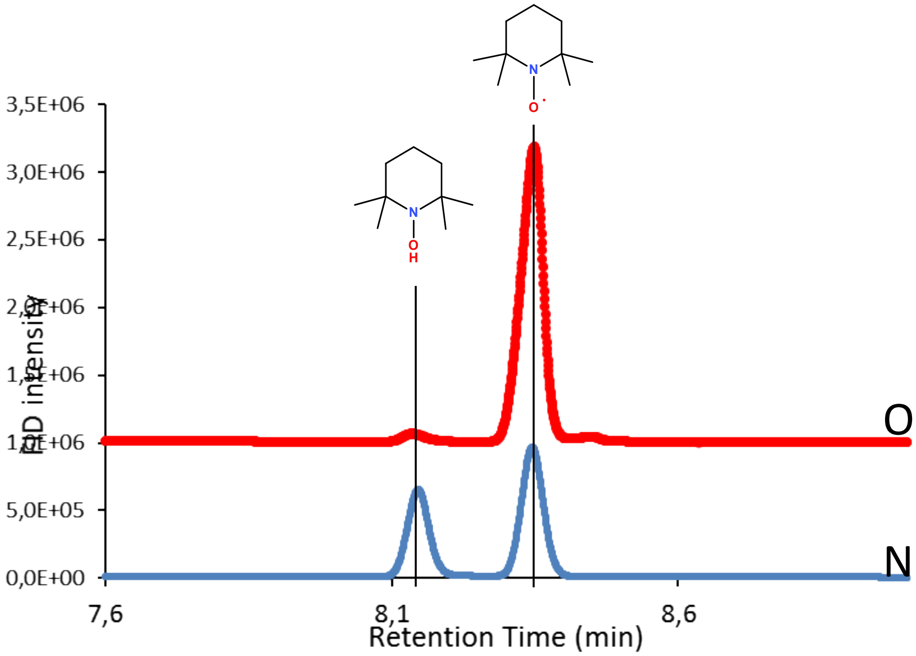

Figure S35 Gas chromatograms showing the accumulation of 1-hydroxy-2,2,6,6-tetramethylpiperidine (TEMPOH) under inert atmosphere (10 mol% Ce, 30 mol% TEMPO, pure benzylalcohol, 110 °C, 7h). Under an O_2 atmosphere, reoxidation of TEMPOH to TEMPO occurs rapidly.

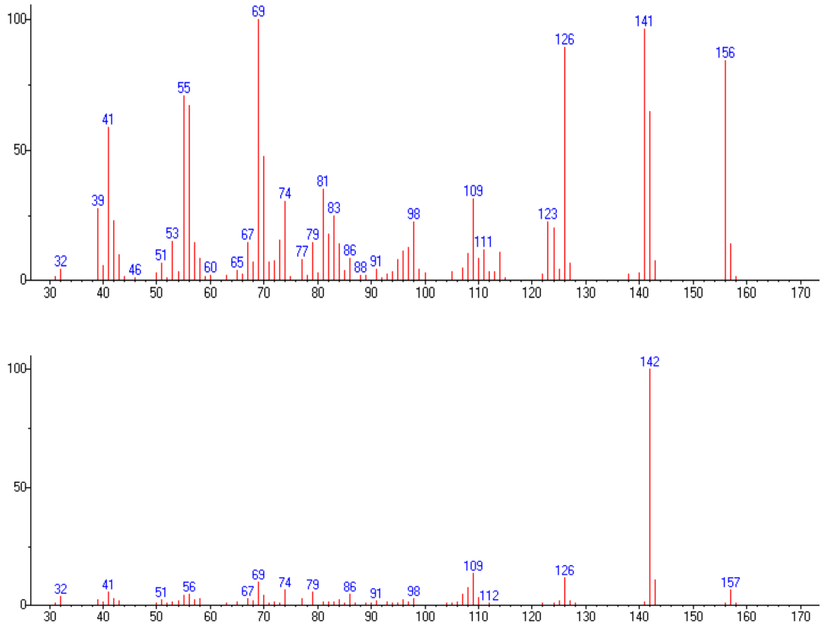

Figure S36 Observed mass spectra for TEMPO (top) and 1-hydroxy-2,2,6,6-tetramethylpiperidine (TEMPOH; bottom).

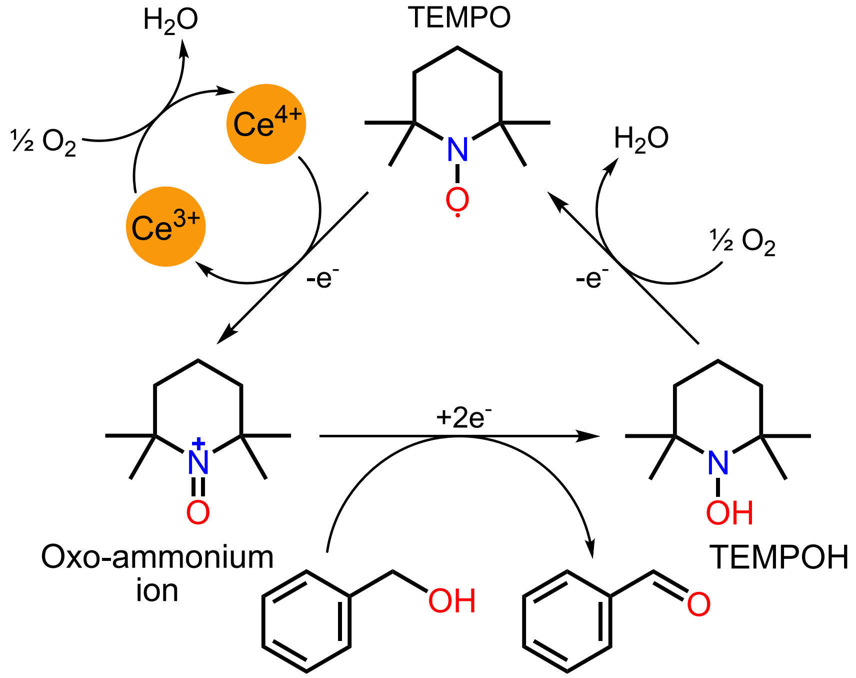

Figure S37 Proposed reaction scheme for the Ce-UiO-66-BDC/TEMPO catalyzed aerobic oxidation of benzyl alcohol.

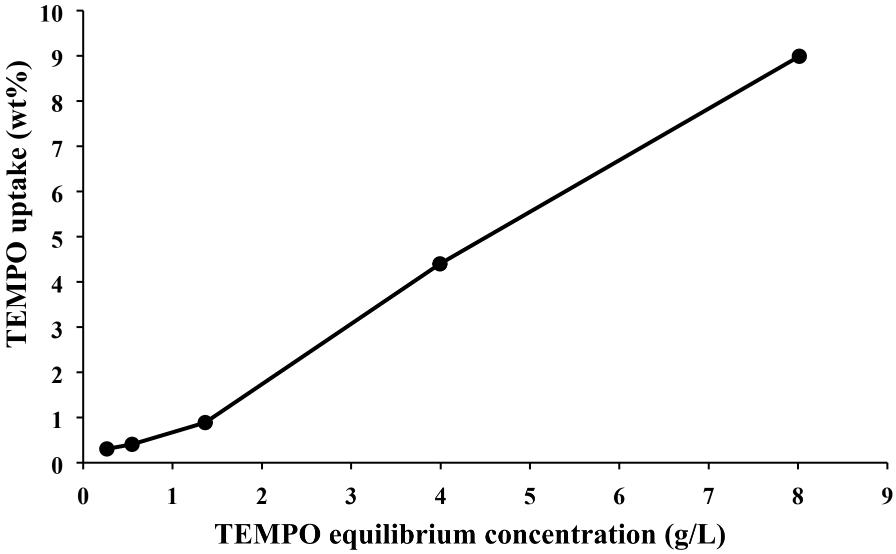

Figure S38 Single-compound adsorption isotherm of TEMPO from CH_3CN on Ce-UiO-66-BDC at 25 °C. TEMPO concentrations applied during benzyl alcohol oxidation range between 2 and 4 g/L.

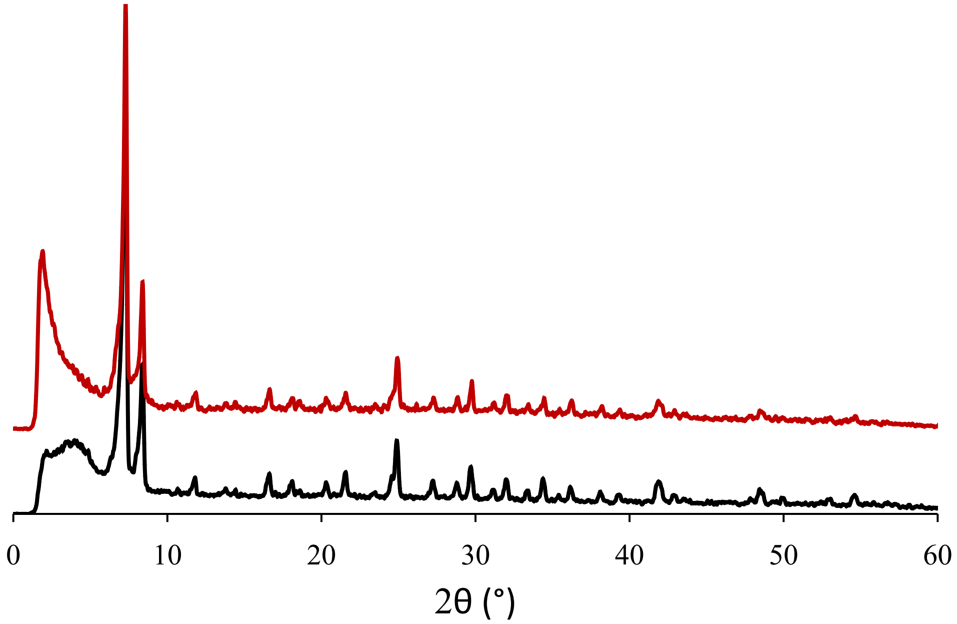

Figure S39 Powder X-ray diffraction patterns of Ce-UiO-66-BDC before (blue) and after (red) benzyl alcohol oxidation.

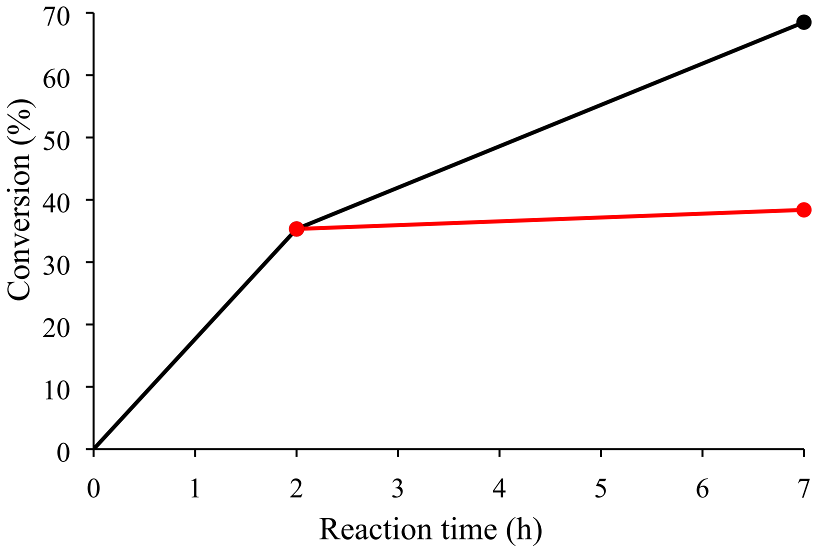

Figure S40 Hot filtration test for the Ce-UiO-66-BDC/TEMPO system in the oxidation of benzyl alcohol. Heterogeneous reaction in black, reaction of filtrate taken at 2 h in red.

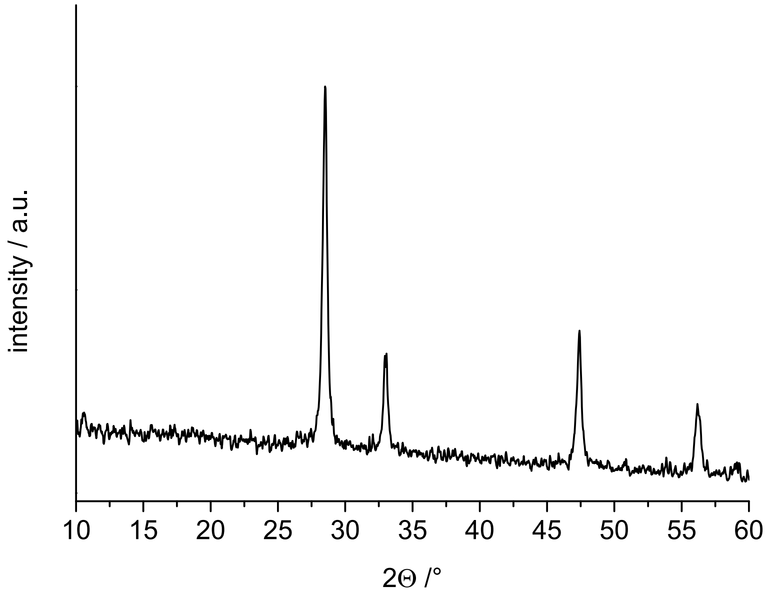

Figure S40 Powder X-ray diffraction pattern of the nanoparticulate CeO_2 (Alfa Aesar, 15-30 nm) used in the study.

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[2] *Materials Studio v4.3*; Accelrys: San Diego, U.S.A.; Cambridge, UK; Tokio, Japan, 2008.

[3] C. Henning, A. Ikeda-Ohno, W. Kraus, S. Weiss, P. Pattison, H. Emerich, P. M. Abdala and A. C. Scheinost, *Inorg. Chem.* 2013, **52**, 11734-11743.

[4] Carlson, S.; Clausen, M.; Gridneva, L.; Sommarin, B.; Svensson, C. J. Synchrotron Radiat. 2006, 13, 359-364.