Electronic Supplementary Material (ESI) for ChemComm.

Experimental details

Synthesis

Synthesis of glycinate/nitrate-capped Ce_6 clusters $[Ce_6O_4(OH)_4(NH_3CH_2COO)_8(NO_3)_4(H_2O)_6Cl_8 \cdot 8H_2O]$ was scaled up from a previously reported protocol.[1] First, 30g cerium ammonium nitrate (CAN; 55 mmol) and 9g glycine (120 mmol) were dissolved in 27g water. To this, 321g of a saturated NaCl solution was added and the resulting solution was left at room temperature for 48h. The formed yellow crystals were filtered off and dried at 60°C (yield: 93%).

Ce-PCN-224(Zn) was synthesized in a 7 mL Pyrex vial. First, 30 mg Ce_6 clusters (77 µmol Ce) was added to 300 µL water and the obtained suspension was immediately added to a solution of 13 mg Zn-tetrakis(*p*-benzoic acid)porphyrin (H_4TCPP(Zn)) (15 µmol) and 300 mg benzoic acid (2459 µmol) in 1.2 mL *N,N'*-dimethylformamide (DMF). This mixture was then placed in a preheated aluminum block at 100°C while stirred at 300 rpm. After 15 minutes, the precipitate was removed from the mother liquor by centrifugation. Metal-free and Sn containing Ce-PCN-224 were synthesized accordingly with equimolar amount of linker.

Ce-MOF-545(Sn) was synthesized in a 7 mL Pyrex vial. First, 26 mg Ce clusters (67 µmol Ce) was added to 300 µL water and the obtained suspension was immediately added to a solution of 13 mg H_4TCPP-$SnCl_2$ (13 µmol, H_4TCPP-$SnCl_2$ synthesized according to literature[2]) and 300 mg benzoic acid (2459 µmol) in 1.2 mL *N,N'*-diethylformamide (DEF). This mixture was then placed in a preheated aluminum block at 100°C while stirred at 300 rpm. After 15 minutes, the precipitate was removed from the mother liquor by centrifugation.

Ce-NU-1000 was synthesized in a 7 mL Pyrex vial. First, 23.5 mg Ce clusters (60 µmol Ce) was added to 250 µL water and the obtained suspension was immediately added to a solution of 10 mg 1,3,6,8-tetrakis(*p*-benzoic aicd)pyrene (H_4TBAPy) (16 µmol) and 675 mg benzoic acid (5533 µmol) in 1.2 mL DMF. This mixture was then placed in a preheated aluminum block at 100°C while stirred at 300 rpm. After 15 minutes, the precipitate was removed from the mother liquor by centrifugation.

Ce-CAU-24-TBAPy was synthesized in a 7 mL Pyrex vial. First, 23.5 mg Ce clusters (60 µmol Ce) was added to 250 µL water and the obtained suspension was immediately added to a solution of 10 mg H_4TBAPy (16 µmol) and 675 mg benzoic acid (5533 µmol) in 1.2 mL DEF. This mixture was then placed in a preheated aluminum block at 100°C while stirred at 300 rpm. After 15 minutes, the precipitate was removed from the mother liquor by centrifugation.

The already reported Ce-UiO-66 analogues were synthesized using an adapted literature procedure.[3] First, 82 mg clusters (210 µmol Ce) were added to 400 µL water and the obtained suspension was immediately added to a solution of 420 µmol linker (H_2Fum, H_2BDC, H_2NDC and H_2BPDC) in 1.2 DMF. This mixture was then placed in a preheated aluminum block at 100°C while stirred at 300 rpm. After 15 minutes, the precipitate was removed from the mother liquor by centrifugation.

Ce-UiO-66-Muc was synthesized using an adapted literature procedure.[3] First, 32 mg clusters (82 µmol Ce) were added to 150 µL water and the obtained suspension was immediately added to a solution of 35 mg muconic acid (246 µmol) and 425 µL acetic acid (7437 µmol) in 1 mL DMF. This mixture was then placed in a preheated aluminum block at 100°C while stirred at 300 rpm. After 15 minutes, the precipitate was removed from the mother liquor by centrifugation.

Ce-UiO-66-CDC was synthesized using an adapted literature procedure.[3] First, 39 mg clusters (100 µmol Ce) were added to 250 µL water and the obtained suspension was immediately added to a solution of 25 mg *trans*-1,4-cyclohexanedicarboxylate (H_2CDC) (145 µmol) and 15 µL acetic acid (263 µmol) in 1 mL DMF. This mixture was then placed in a preheated aluminum block at 100°C while stirred at 300 rpm. After 15 minutes, the precipitate was removed from the mother liquor by centrifugation.

Material Characterization

High quality synchrotron powder X-ray diffraction (PXRD) data were obtained at the beamline BM11 of Argonne National Laboratory with a wavelength $\lambda = 0.412628$ Å and a resolution of 0.001° 2θ. The detector consists of 12 independent Si(111) analyzer crystals and $LaCl_3$ scintillation detectors that are separated by approximately 2° 2θ.

Powder X-ray diffraction patterns were recorded on a STOE STADI P diffractometer (monochromated $CuK_{\alpha1}$-radiation) equipped with a Mythen detector in transmission geometry.

Powder X-ray diffraction patterns of the already reported Ce-UiO-66 analogues and materials after stability tests were recorded on a STOE COMBI P diffractometer (monochromated $CuK_{\alpha1}$-radiation) equipped with an IP-PSD detector in transmission geometry. All diffraction data was analyzed using TOPAS 5.[4]

Thermogravimetric analyses were performed on a TA instruments TGA Q500. Samples were heated at a rate of 10 °C min^{-1} to 700 °C under an O_2 flow.

N_2 sorption measurements were performed on a Micromeritics 3Flex surface analyzer at -196°C. Prior to measurements, samples were evacuated under vacuum at room temperature for 12 hours. Surface areas were calculated using the multi-point BET method applied to the isotherm adsorption branch.

Metal content was determined by ICP-AES on an Ultima spectrometer (Horiba Scientific). Samples (50 mg) were dissolved in HNO_3 (65%) prior to analysis.

Liquid ^{1}H-NMR was performed by digesting 10 mg sample in 600 µL deuterated dimethyl sulfoxide (DMSO-d_6) and 10 µL 40wt% hydrofluoric acid in water. The NMR spectra were obtained on a 300 MHz Bruker Avance spectrometer.

Catalytic experiments

A mixture of 34 mg (0.225 mmol) 2,2,6,6-Tetramethyl-1-piperidinyloxy, 78 µL (0.75 mmol) benzyl alcohol and 76 µL (0.75 mmol) chlorobenzene in 8 mL acetonitrile was added to 21 mg (0.037 mmol; 5 mol% with respect to benzyl alcohol) Ce-MOF-545(Sn) in a 10 mL stainless steel reactor equipped with a pressure gauge. The reactor was subsequently flushed three times with oxygen and finally charged with 6 bar oxygen after which reaction proceeded at 110°C under stirring (500 rmp) for seven hours. After reaction, the reactor was allowed to cool down in an ice bath and the oxygen pressure was subsequently released. The reaction mixture was then centrifuged and analyzed using GC.

Structure Determination

Due to the sensitivity of the MOF materials towards pore evacuation, all PXRD patterns were measured on solvent-filled samples. This inhibited a full Rietveld refinement of the diffraction data as the disordered electron density in the pores could not be fitted to a satisfactory extent, with the exception of Ce-MOF-545(Sn) which could be modeled using Rietveld methods. For the refinement of Ce-MOF-545(Sn), a crystalline by-product exhibiting the Ce-MOF-525(Sn) structure was taken into account (~10 wt%) for which only the cell parameters and temperature factors were refined. For the framework of Ce-MOF-545(Sn), a suitable framework model was generated using Materials Studio[5] after imposing the unit cell parameters that were extracted from a Le Bail fit. The positions of the tin, chlorine and cerium atoms as well as the positions of the oxygen atoms inside the cluster were refined while the position of the linker molecules was fixed. The pore content had to be modelled using 18 dummy oxygen atoms as well as one dummy cerium atom as placeholders for the disordered electron density originating from adsorbed guest species. Moreover a strong preferred orientation along (010) was also modelled and a spherical harmonics correction was employed to model the anisotropic peak broadening. Taking all these corrections into account, the crystallographic accuracy of the resulting model is comparably low but still indicates a framework isostructural to MOF-545. The refinement converged to sufficient figures of merit (Table S1). For Ce-PCN-224(Zn), Ce-NU-1000 and Ce-CAU-24-TBAPy Le Bail refinements resulted in acceptable figures of merit (Table S1). The PXRD pattern of Ce-PCN-224(Zn) displayed extra reflections at 1.97, 2.19, 2.50, 3.02, 3.94, 4.02 and 8.44 ° 2θ, which indicates the presence of trace impurities. These reflections could not be assigned to any known phase and were omitted from the final Le Bail fit.

Table S1. Crystallographic data of Ce-PCN-224(Zn), Ce-MOF-545(Sn), Ce-NU-1000 and Ce-CAU-24-TBAPy.

compound	**Ce-PCN-224(Zn)**	**Ce-MOF-545(Sn)**	**Ce-NU-1000**	**Ce-CAU-24-TBAPy**
refinement	Le Bail	Rietveld	Le Bail	Le Bail
Space group	*Im-3m*	*P6/mmm*	*P6/mmm*	*Cmmm*
a / Å	39.3479(5)	43.3623(10)	40.2727(192)	24.0614(66)
b / Å	39.3479(5)	43.3623(10)	40.2727(192)	33.0148(34)
c / Å	39.3479(5)	17.2006(7)	16.9003(63)	16.5931(25)
R_{wp} / %	10.2	9.7	6.9	4.4
R_{Bragg} / %	-	3.4	-	-
GoF	2.5	3.0	2.3	1.9

Hexanuclear glycinate/nitrate capped Ce clusters

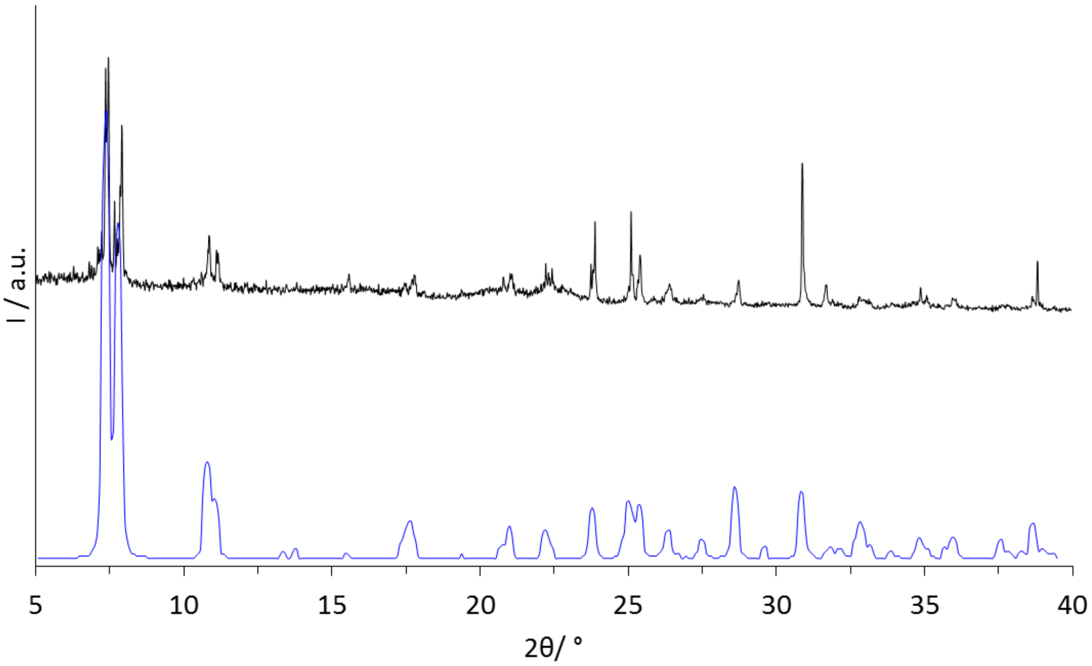

Figure S1. Experimental (black) and literature (blue) PXRD pattern of Ce_6 precursor clusters (λ = 1.540562 Å).[1]

Ce-UiO-66 analogues

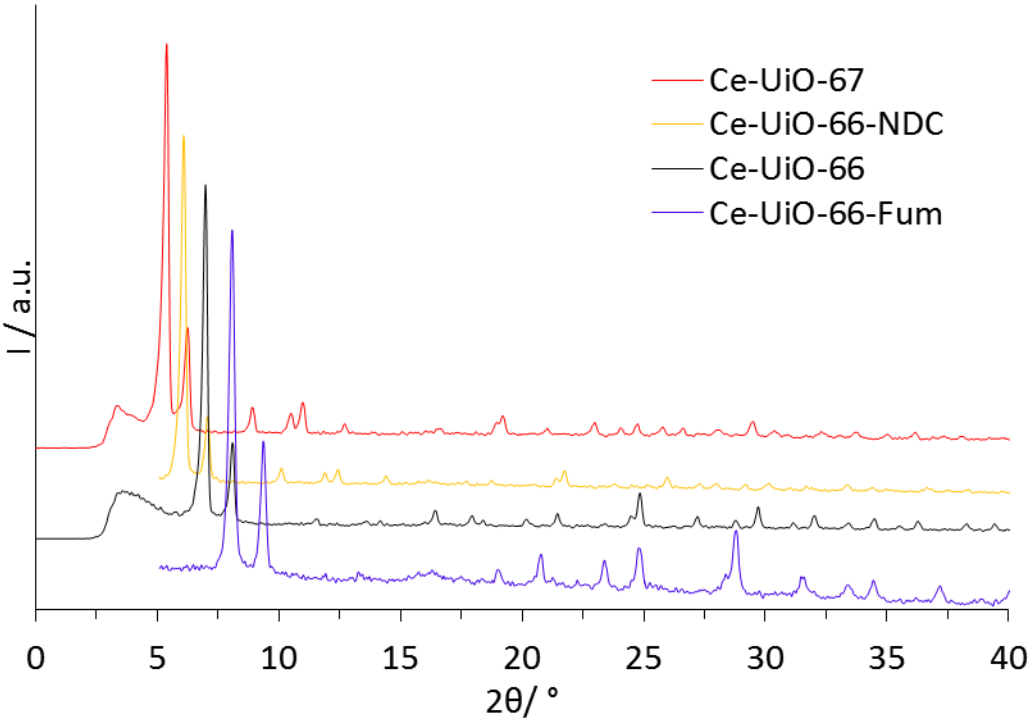

Figure S2. PXRD pattern of four existing Ce-MOFs synthesized starting from Ce_6 precursor clusters: Ce-UiO-66-Fum (blue), Ce-UiO-66 (black), Ce-UiO-66-NDC (yellow) and Ce-UiO-67 (red) (λ = 1.540562 Å).

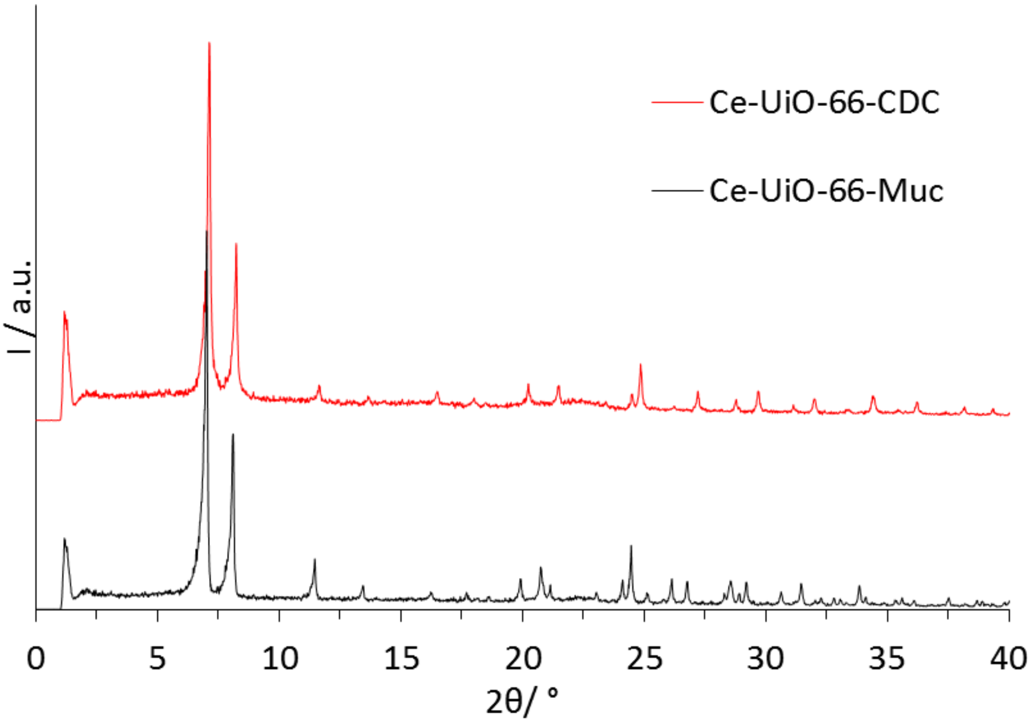

Figure S3. PXRD pattern of two newly synthesized Ce analogues of UiO-66 with aliphatic linkers: Ce-UiO-66-CDC (red) and Ce-UiO-66-Muc (black) (λ = 1.540562 Å).

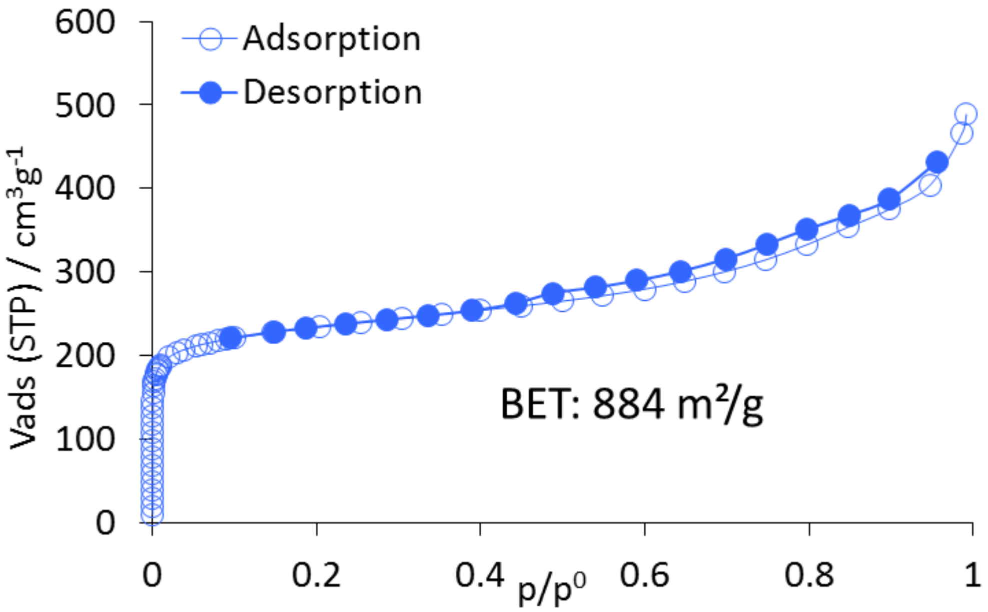

Figure S4. Nitrogen physisorption isotherm of Ce-UiO-66 synthesized from clusters.

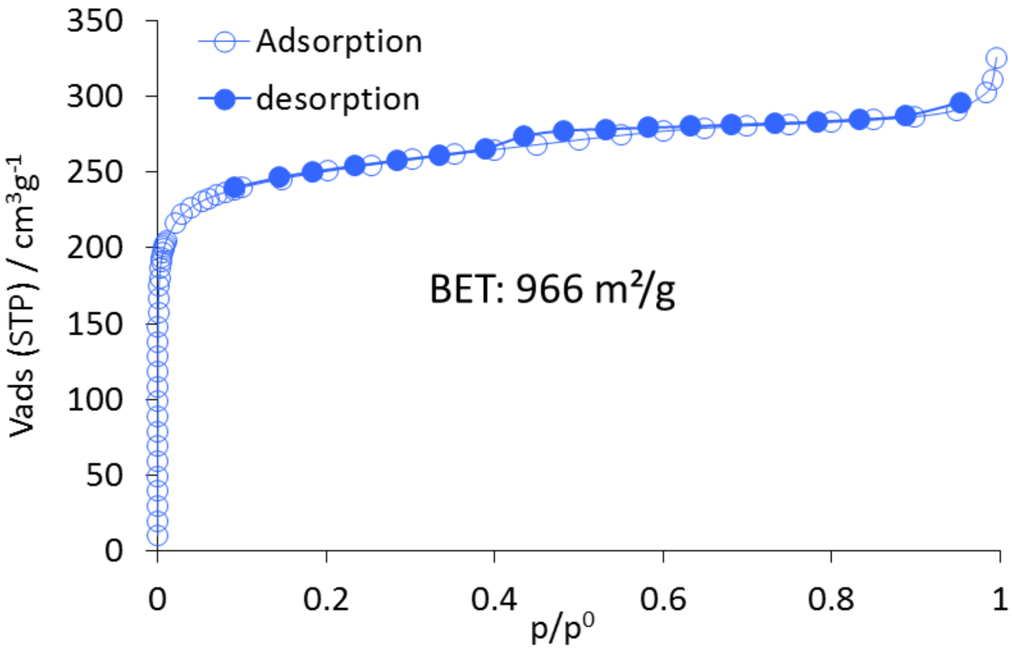

Figure S5. Nitrogen physisorption isotherm of Ce-UiO-66-Muc.

Ce-PCN-224

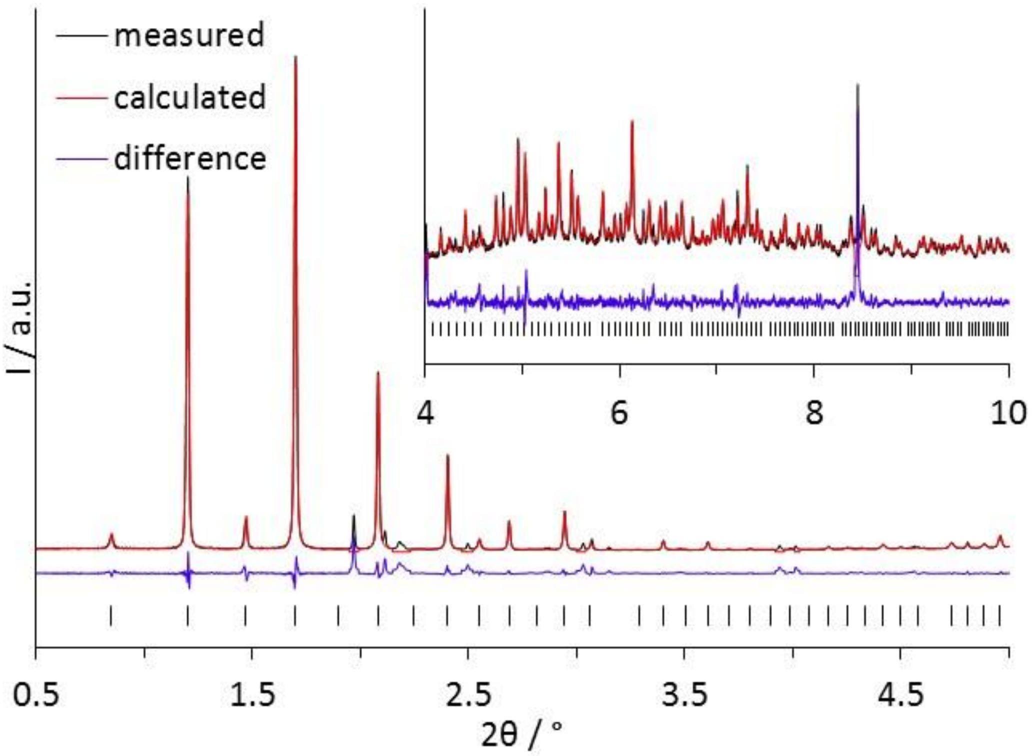

Figure S6. Le Bail refinement of Ce-PCN-224(Zn) (λ = 0.412628 Å). Sample is measured at BM-11 of Argonne National Laboratory.

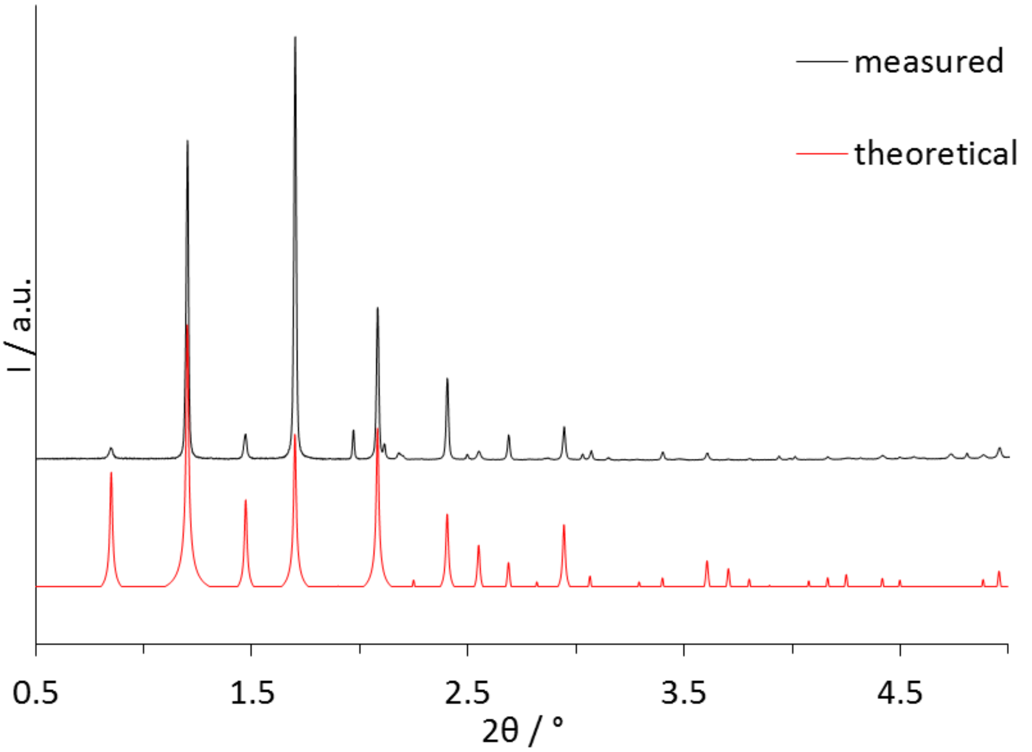

Figure S7. Experimental and theoretical PXRD pattern of Ce-PCN-224(Zn) (λ = 0.412628 Å). Sample is measured at BM-11 of Argonne National Laboratory.

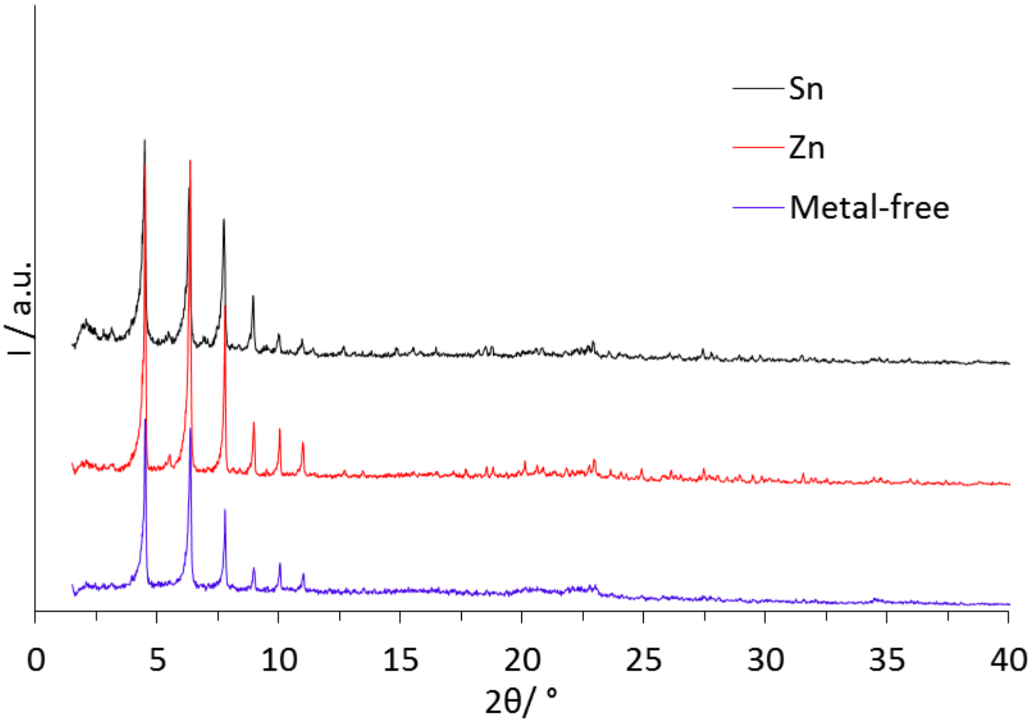

Figure S8. PXRD pattern of Ce-PCN-224 with Sn (black), Zn(red) or metal-free (blue) (λ = 1.540562 Å).

Ce-NU-1000

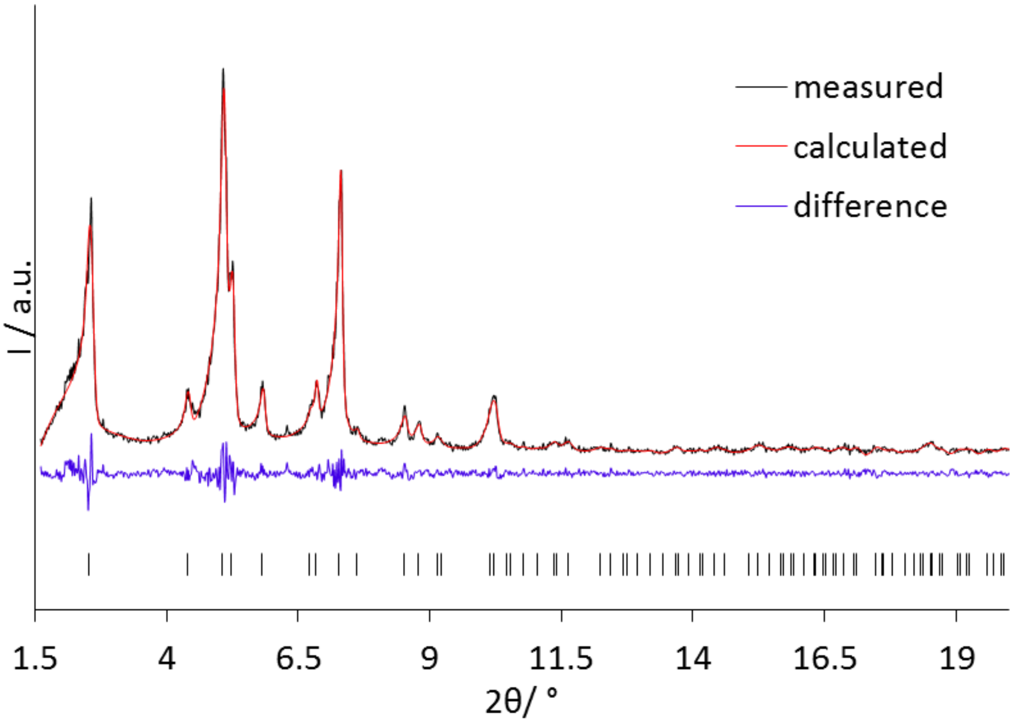

Figure S9. Le Bail refinement of Ce-NU-1000 (λ = 1.540562 Å).

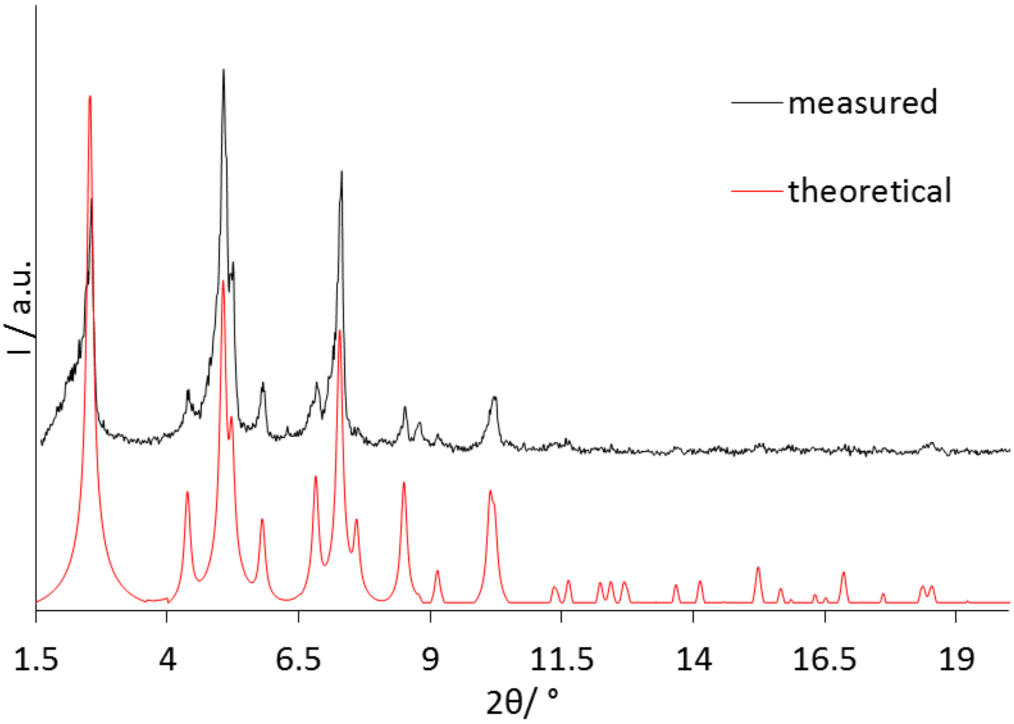

Figure S10. Experimental and theoretical PXRD pattern of Ce-NU-1000 (λ = 1.540562 Å).

Ce-CAU-24-TBAPy

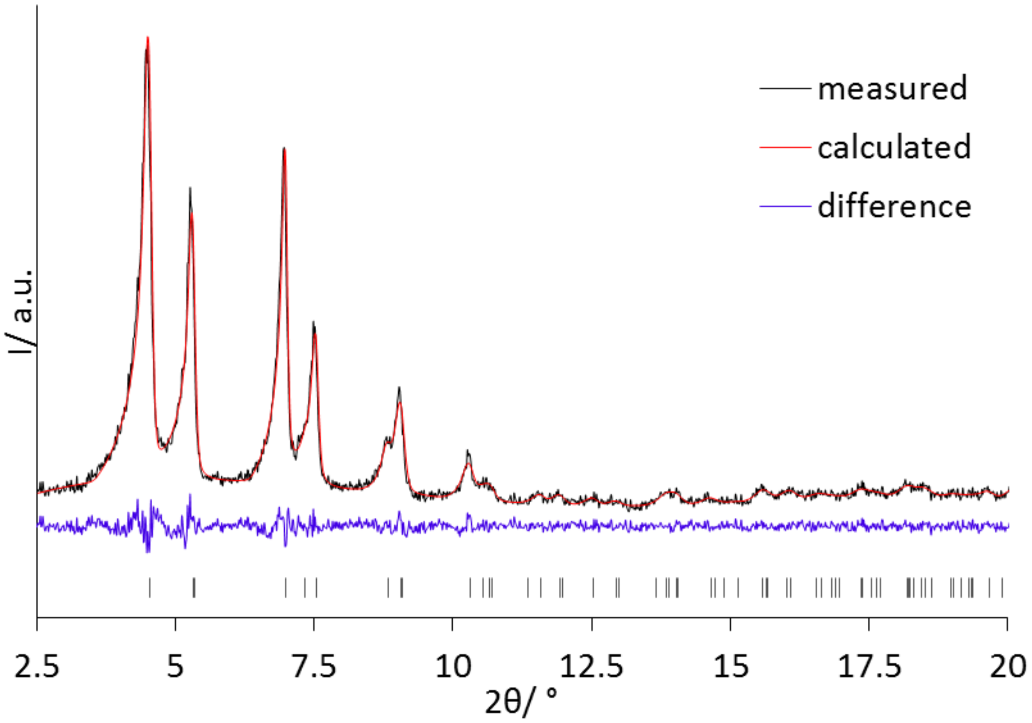

Figure S11. Le Bail refinement of Ce-CAU-24-TBAPy (λ = 1.540562 Å).

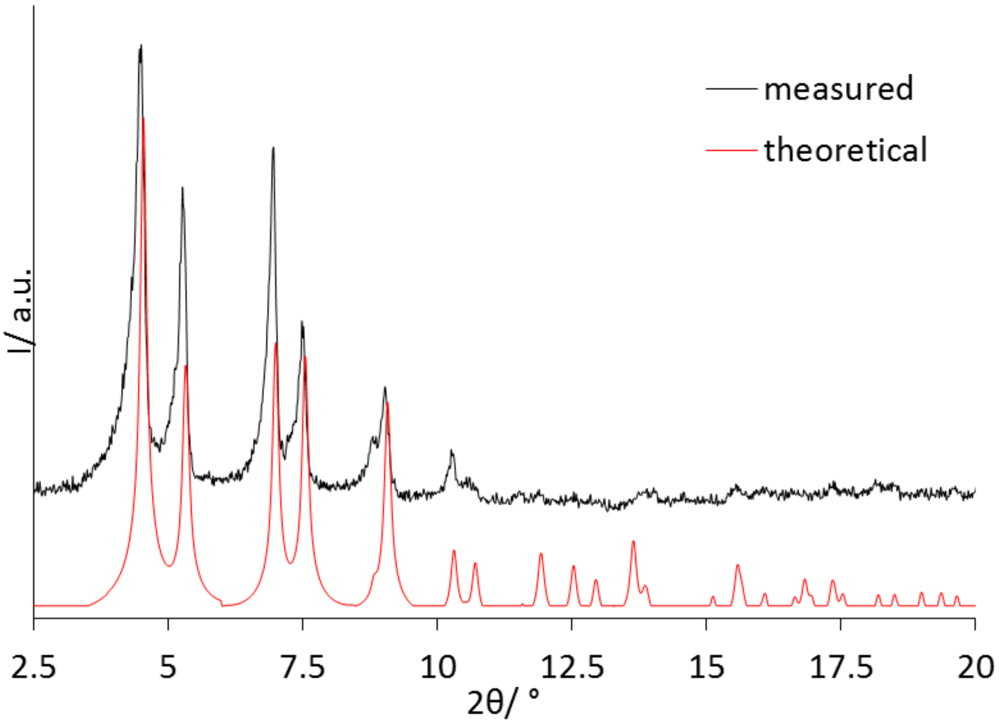

Figure S12. Experimental and theoretical PXRD pattern of Ce-CAU-24-TBAPy (λ = 1.540562 Å).

CAU-19

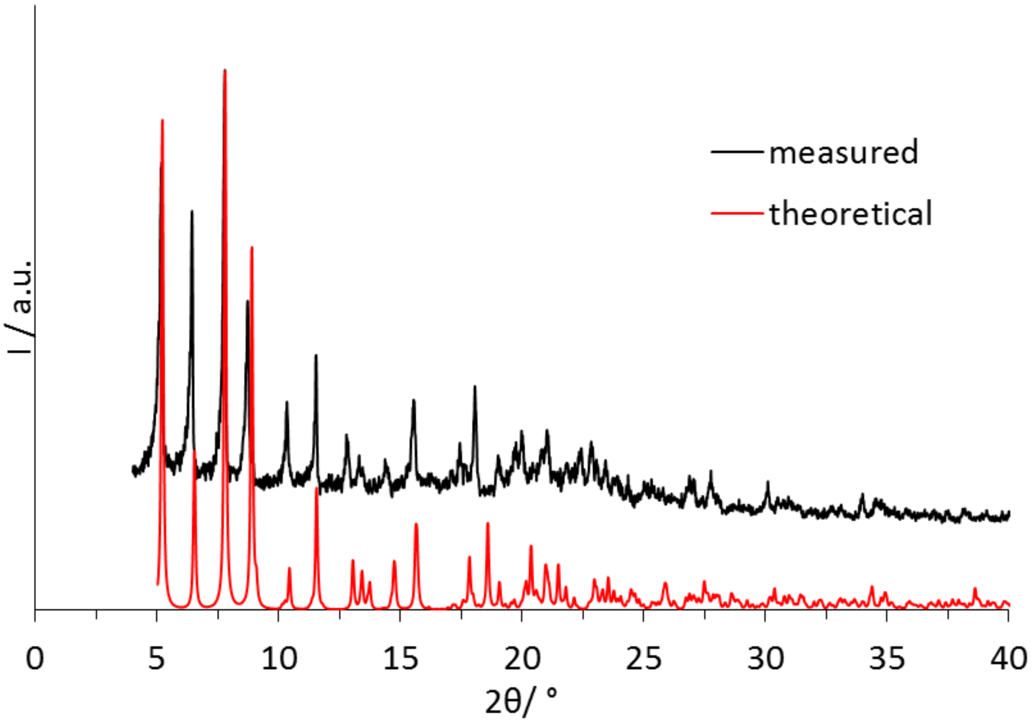

Figure S13. PXRD pattern of CAU-19 obtained after prolonged synthesis of Ce-MOF-545 (λ = 1.540562 Å).[6]

NMR

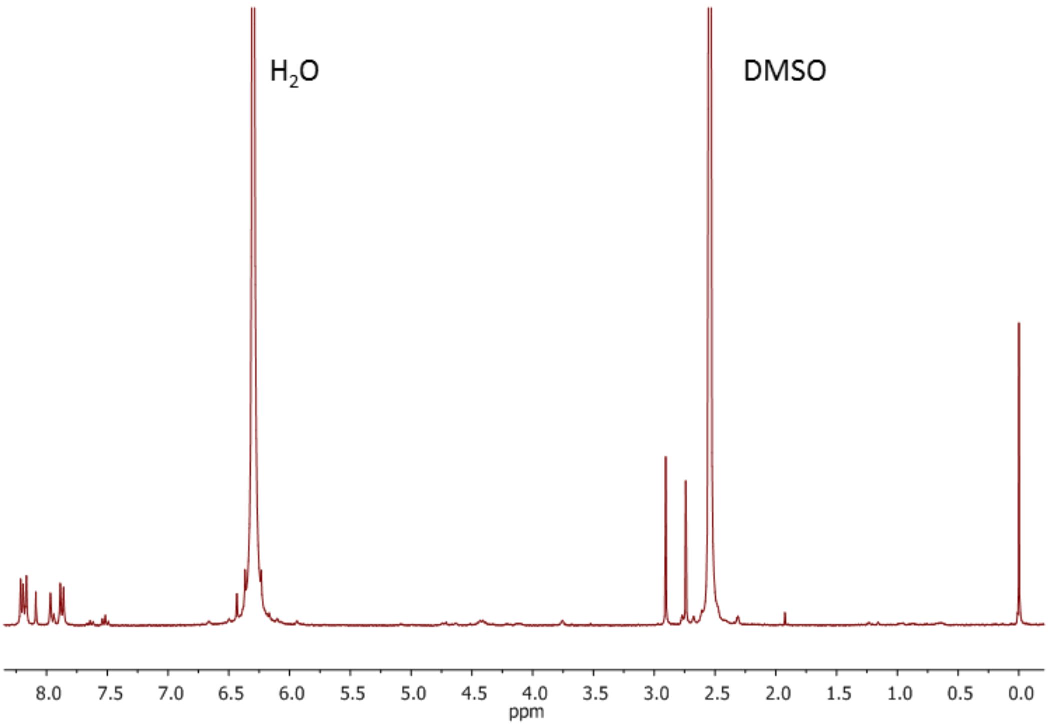

Figure S14. Liquid ^1H NMR spectrum of digested Ce-NU-1000 in deuterated DMSO. Absence of a peak at 3.6 ppm confirms that all glycinate on the precursor was exchanged during synthesis and that no residual capping agents are present in the material.

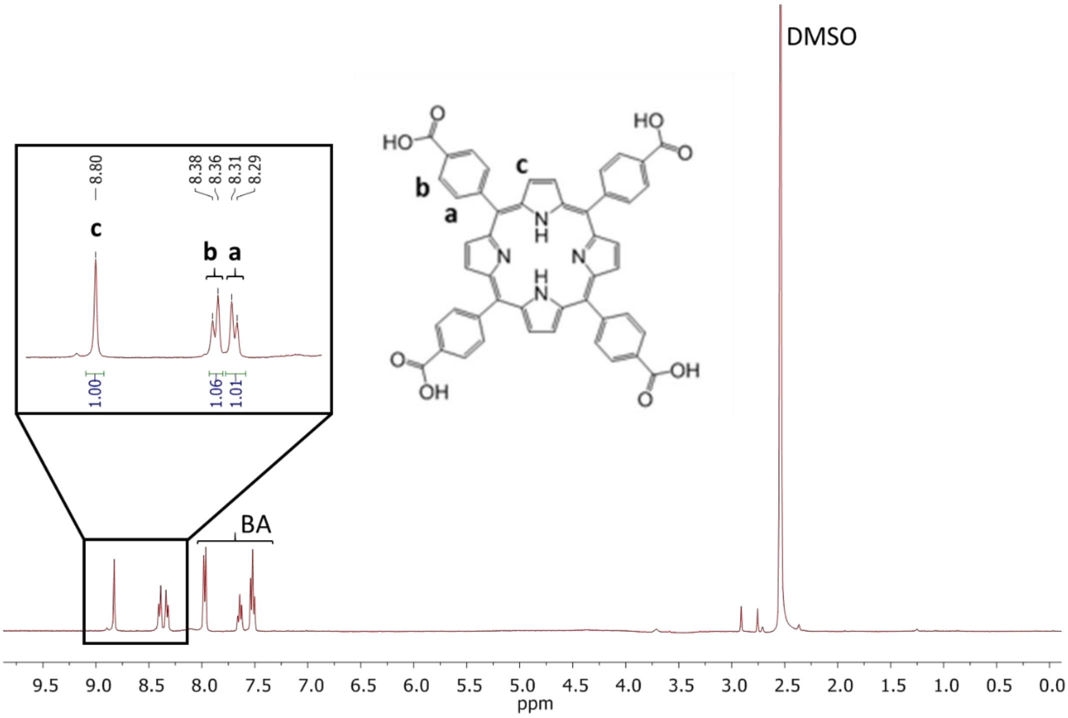

Figure S15. Liquid ^1H NMR spectrum of digested Ce-PCN-224(Zn) in deuterated DMSO: δ 8.34 ppm (d, 8H), 8.39 ppm (d,8H) and 8.86 ppm (s,8H) c. Absence of a peak at 3.6 ppm confirms that all glycinate on the precursor was exchanged during synthesis and that no residual capping agents are present in the material.

Stability tests

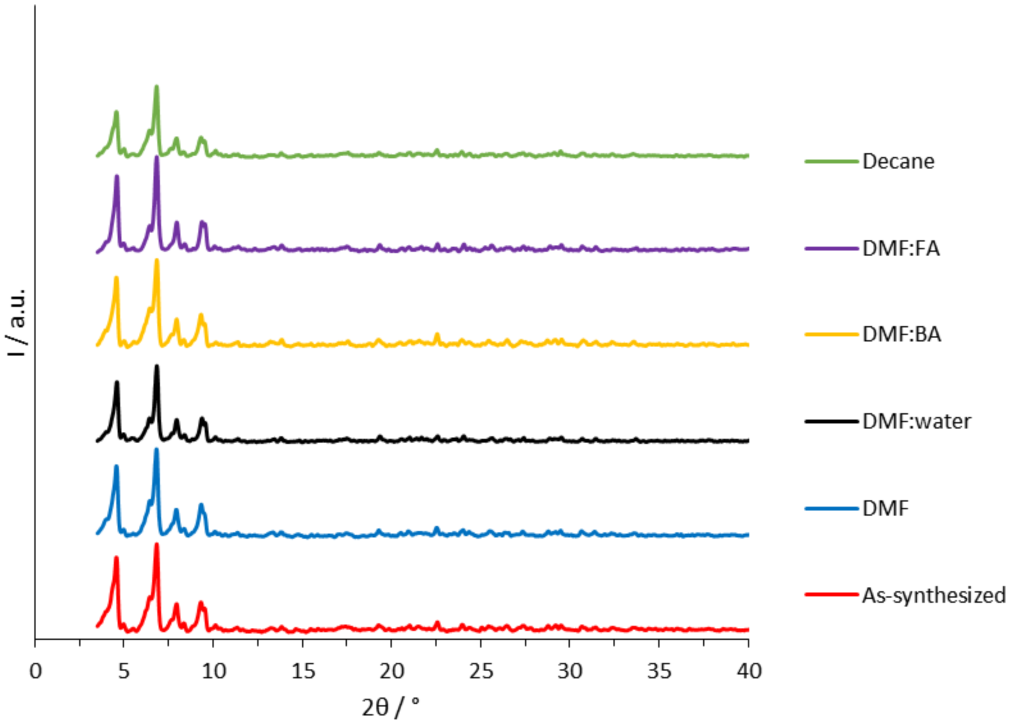

Figure S16. PXRD patterns of Ce-MOF-545(Sn) after suspension in different solvents (λ = 1.540562 Å).

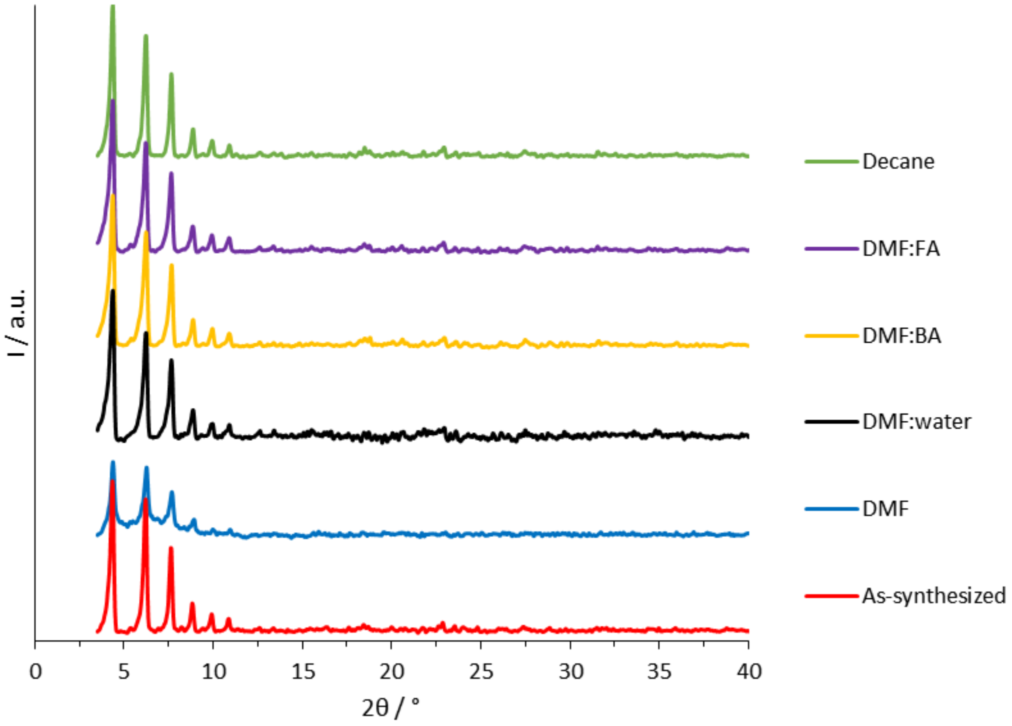

Figure S17. PXRD pattern of Ce-PCN-224(Zn) after suspension in different solvents (λ = 1.540562 Å). A decrease in crystallinity is observed for the material suspended in DMF.

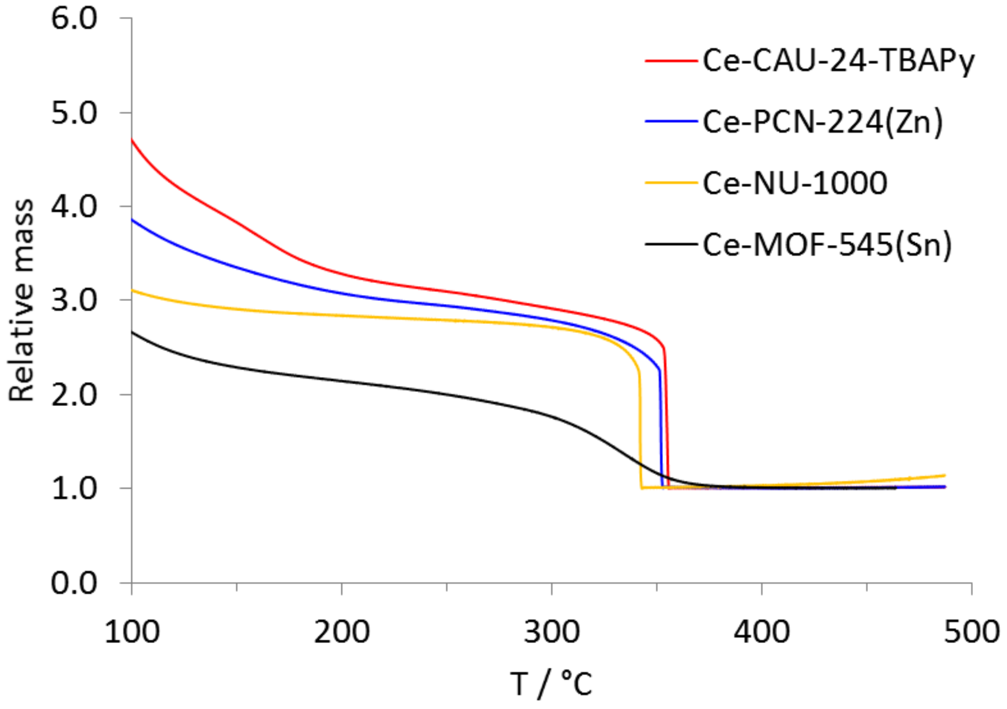

Figure S18. Thermogravimetric analysis of Ce-CA-24-TBAPy (red), Ce-PCN-224(Zn) (blue), Ce-NU-1000 (yellow) and Ce-MOF-545(Sn) (black). All materials decompose at approximately 350°C.

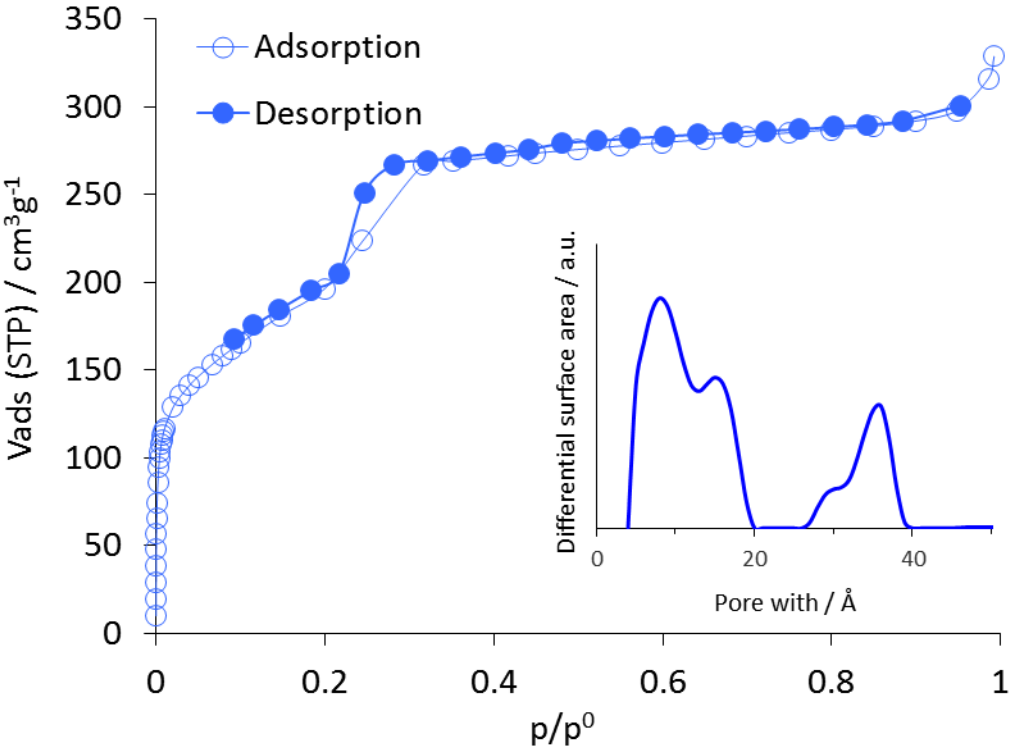

Figure S19. Nitrogen physisorption isotherm of Ce-MOF-545(Sn) after evacuation at room temperature. Tarazona NLDFT calculated differential pore size distribution in inset is in good agreement with crystallographic data, indicating that Ce-MOF-545(Sn) is reasonably stable upon evacuation.

Table S2. Elemental analysis of all novel Ce-MOFs

	Ce / wt%	**Zn / wt%**	**Sn / wt%**
Ce-UiO-66-Muc	**39.7**	**0**	**0**
Ce-UiO-66-CDC	**41.9**	**0**	**0**
Ce-PCN-224(Zn)	**27.3**	**3.2**	**0**
Ce-MOF-545(Sn)	**25.8**	**0**	**5.1**
Ce-NU-1000	**30.8**	**0**	**0**
Ce-CAU-24-TBAPy	**25.5**	**0**	**0**

References

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