The first water-based synthesis of Ce(IV)-MOFs with saturated chiral and achiral C₄-dicarboxylate linkers

Jannick Jacobsen,^a Bastian Achenbach,^a Helge Reinsch,^a Simon Smolders,^b Florian-David Lange,^c Gernot Friedrichs,^c Dirk De Vos,^b and Norbert Stock ^{*,a}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Six different chiral and achiral alkane dicarboxylic C₄-acids, i.e. succinic acid (H₂SUC), DL-2-methylsuccinic acid (H₂MS), 2,3-dimethylsuccinic acid (H₂DMS) and aspartic acid (D-, L- and DL-H₂ASP), were used to obtain Ce(IV)-MOFs via microwave assisted reactions. In water-based syntheses, MOFs with three different topologies, denoted as UiO-66 (**fcu**), CAU-41 (**bct**) and CAU-44 (**bct**), were obtained within 30 min under mild reaction conditions. The MOFs were fully characterized and their structures were refined from PXRD data. The chirality of the incorporated linker molecules was confirmed by circular dichroism spectroscopy. The optical activity was also investigated by second-harmonic generation (SHG) measurements. The use of H₂MS, H₂DMS and H₂ASP leads to the formation of a UiO-66 structure, and a hydrated form of the usual hexanuclear cluster, i.e. [Ce₆(μ₃-O)₄(μ₃-OH)₄(H₂O)₆]¹²⁺ was observed. Rietveld refinement of the PXRD data showed an ordered arrangement of the D- and L-enantiomers in Ce-UiO-66-DL-ASP. By employing H₂Suc as the linker, the other two title compounds are obtained. CAU-41, [Ce₆(μ₃-O)₄(μ₃-OH)₄(SUC)₄(OH)₄(H₂O)₄], exhibits the well-known eight-fold connectivity of the hexanuclear cluster, whereas in CAU-44, [Ce₆(μ₃-O)₄(μ₃-OH)₄(SUC)₄(NO₃)₂(OH)₂(H₂O)₂], the connection of the clusters is also achieved by nitrate ions resulting in a framework with **bct** topology.

Introduction.

Metal-organic frameworks (MOFs) are porous coordination polymers formed by connecting organic (linker) and inorganic building units (IBUs). They often exhibit high specific surface areas, tunable pore sizes and diverse chemical functionalities.^{1–3} These properties make them suitable for potential applications like gas separation, catalysis and heat transformation.^{4–6} The most popular Zr-MOF, Zr-UiO-66, is based on hexanuclear [Zr₆(μ₃-O)₄(μ₃-OH)₄]¹²⁺ clusters which are ideally connected by twelve terephthalate (BDC²⁻) linker molecules to form a three-dimensional network with **fcu** topology and composition [Zr₆(μ₃-O)₄(μ₃-OH)₄(BDC)₆].⁷ Since the discovery of UiO-66, the popularity of Zr-MOFs has increased continuously⁸ due to their high thermal and chemical stability.⁹ Because of structural defects, the BET surface areas of Zr-UiO-66 range from 1080 to 1580 m²g⁻¹.^{10–12} These can be controlled via the synthesis conditions.^{11,13} In more recent years the synthesis of MOFs containing other tetravalent metal ions has been also investigated. The UiO-66 structure type can be

built up with hafnium(IV)¹⁴, cerium(IV)⁴, uranium(IV)¹⁵, thorium(IV)¹⁶ and neptunium(IV).¹⁷ In addition some isorecticular compounds with a variety of functionalized terephthalic acids^{4,10,18,19} and linear linker molecules^{7,20,21} were used to synthesize the UiO-66 structure type. Especially the Ce(IV)-based MOFs have attracted scientific interest due their redox chemistry.^{4,22} The MOF Ce-UiO-66-BDC was successfully tested as an oxidation catalyst,⁴ for detoxification of nerve agents²³ and it was used as precursor for the preferential CO oxidation in combination with CuO.²⁴ In addition to UiO-66 (**fcu** topology), other Ce(IV)-MOFs, based on the hexanuclear [Ce₆(μ₃-O)₄(μ₃-OH)₄]¹²⁺ cluster were reported, i. e. MOF-808 (**spn**)²⁵, NU-1000 (**csq**)²⁶ and CAU-24 (**scu**).²⁷ Furthermore, the catalytic activity of Ce-MOF-808 was tested.²² All of these Ce(IV)-based MOFs were synthesized by similar approaches in different mixtures of H₂O and *N,N*-dimethylformamide (DMF), partially including small amounts of modulator. Ce-UiO-66-PDC²⁸ and Ce-MIL-140a²⁹ are the first pure water-based synthesized Ce(IV)-MOFs. To the best of our knowledge only

Figure 1. Overview of the four flexible aliphatic linker molecules used for the synthesis of Ce(IV)-based MOFs. For H₂ASP a racemic mixture as well as the pure enantiomers were used.

^a Institute of Inorganic Chemistry, Christian-Albrechts-Universität zu Kiel, Max-Eyth Straße 2, 24118 Kiel, Germany. E-Mail: stock@ac.uni-kiel.de

^b Centre for Surface Chemistry and Catalysis, KU Leuven, Celestijnenlaan 200F p.o. box 2461, 3001 Leuven, Belgium E-Mail: dirk.devos@kuleuven.be

^c Institute of Physical Chemistry, Christian-Albrechts-Universität zu Kiel, Max-Eyth Straße 1, 24118 Kiel, Germany. E-Mail: friedrichs@phc.uni-kiel.de

Electronic Supplementary Information (ESI) available: PXRD patterns, Rietveld refinements, crystallographic data, circular dichroism spectroscopy, TGA data, CHNS analysis N₂ sorption measurements, ¹H-NMR and IR spectroscopy.

CCDC Numbers: 1909174 – 1909176

See DOI: 10.1039/x0xx00000x

one Ce(IV)-based MOF was synthesized without aromatic linker molecules (Ce-UiO-66-Fum, Fum²⁻ = fumarate).⁴

Table 1. Overview of the optimized synthesis conditions for the title compounds. The concentration of the aqueous solution of cerium(IV) ammonium nitrate is 0.5333 mol/L. The yield, based on cerium, of each MOF is also given in the last column.

Compound	Ce	Ratio Linker	HCOOH	Ce [mL] 0.533 M	Linker [mg]	H ₂ O [mL]	HCOOH [μ L]	yield [%]
Ce-UiO-66-DL-ASP	1	1.5	145	3	319	9	8760	86
Ce-UiO-66-D-ASP	1	1.5	145	3	319	9	8760	84
Ce-UiO-66-L-ASP	1	1.5	145	3	319	9	8760	89
Ce-UiO-66-MS	1	11	0	3	2325	9	0	86
Ce-UiO-66-DMS	1	2.0	25	2	312	6	1006	70
Ce-CAU-41	1	8.5	10	2	2142	12	804	92
Ce-CAU-44	1	3.5	0	2	936	12	0	97

In addition, no Ce(IV)-MOFs are known yet with flexible aliphatic or chiral linker molecules. Here we report our successful water-based syntheses of Ce(IV)-MOFs with the four flexible aliphatic linkers succinic acid (H₂SUC), 2-methylsuccinic acid (H₂MS), 2,3-dimethylsuccinic acid (H₂DMS) and aspartic acid (D-, L- and DL-H₂ASP) by using microwave supported reactions (Fig. 1).

Experimental.

Materials and Methods

Cerium ammonium nitrate (98 %, (NH₄)₂Ce(NO₃)₆, Alfa Aesar), succinic acid (H₂SUC, 99 %, C₄O₄H₆, abcr GmbH), DL-aspartic acid (H₂ASP, 99 %, C₄O₄H₇N, TCI GmbH), D-aspartic acid (D-H₂ASP, 98 %, C₄O₄H₇N, TCI GmbH), L-aspartic acid (L-H₂ASP, 99 %, C₄O₄H₇N, TCI GmbH), DL-2-methylsuccinic acid (H₂MS, 99 %, C₅O₄H₈, TCI GmbH), 2,3-dimethylsuccinic acid (H₂DMS, 99 %, C₆O₄H₁₀, Sigma Aldrich) and formic acid (99 - 100 %, HCOOH, BASF) were used as obtained.

The synthesis optimization process of each title compound was carried out in an Anton Paar Synthos 3000 microwave oven by using high-throughput methods.^{30,31} The products were synthesized in glass tubes (max. Volume = 3 mL) under stirring. The optimized synthesis conditions were scaled up in a Biotage Initiator⁺ microwave oven by using glass tubes, with a max. volume of 20 mL, for in depth characterisation. Powder X-ray diffraction (PXRD) for product identification was carried out on a Stadi P Combi diffractometer with CuK α_1 radiation (λ = 1.5401). PXRD patterns for Rietveld refinements were recorded on a Stadi MP diffractometer with a MYTHEN detector and CuK α_1 radiation. Sorption experiments were performed using a BEL Japan Inc. Belsorpmax. apparatus. Prior to the sorption experiments all compounds were heated at 60 °C under reduced pressure (10⁻² kPa) for 16 h. The specific surface areas were determined using the Rouquerol method.³² Thermogravimetric measurements were carried out using a Netzsch STA-409CD under air flow (75 mL/min) with a heating rate of 4 K/min between 20 and 800 °C. IR spectra were recorded on a Bruker ALPHA-FT-IR A220/D-01 spectrometer equipped with an ATR-unit. ¹H-NMR spectra were measured on

a Bruker DRX 500 spectrometer. The circular dichroism spectra were measured with a JASCO-1500 spectrometer directly after dissolution. The far-UV (225-250 nm) CD spectra were recorded with a 1 mm quartz cuvette. The resulting spectra were averaged over 5 accumulations with bandwidth of 1 nm. All spectra were corrected for background effects by subtracting the spectrum of a 50 mM NaOH solution. Second-harmonic generation (SHG) activity of the powdered D-, L- and DL-ASP compounds was analyzed with a home-built SHG spectrometer at a fundamental wavelength of 1000 nm. SHG signal intensities were averaged over 5 minutes and have been corrected for weak background signal effects.

Synthesis of the Ce-UiO-66 type compounds

The different linker molecules D-, L- and DL-aspartic acid (D-, L- and DL-H₂ASP), 2-methylsuccinic acid (H₂MS) and 2,3-dimethylsuccinic acid (H₂DMS) were dissolved in distilled water and were introduced into the glass reactor. After the addition of the formic acid (HCOOH) and aqueous solution of cerium(IV) ammonium nitrate (0.5333 mol/L) the reactor was sealed and the reaction was carried out (Tab. 1). The glass reactor was heated up under stirring for 30 min at 100 °C. The obtained product was separated by centrifugation from the mother liquor, which was then decanted off. The product was re-dispersed and centrifuged twice in acetone and dried in air at 70 °C. Before characterization, Ce-UiO-66-ASP, [Ce₆(μ_3 -O)₄(μ_3 -OH)₄(H₂O)₆(DL-ASP)₆], was treated for 24 h in 0.2 M HCl and thereafter in acetone for 24 h under stirring at room temperature, respectively and dried in air at 70 °C. The same procedure was performed with the compounds Ce-UiO-66-D-ASP, [Ce₆(μ_3 -O)₄(μ_3 -OH)₄(H₂O)₆(D-ASP)₆] and Ce-UiO-66-L-ASP, [Ce₆(μ_3 -O)₄(μ_3 -OH)₄(H₂O)₆(L-ASP)₆]. The MOFs Ce-UiO-66-MS and Ce-UiO-66-DMS were treated in acetone for 24 h under stirring at room temperature and dried in air at 70 °C.

Synthesis of CAU-41 and CAU-44

The linker succinic acid was (H₂SUC) dissolved in distilled water and introduced into the glass reactor. After the addition of the formic acid (HCOOH only for CAU-41) and the aqueous solution of cerium(IV) ammonium nitrate (0.5333 M) the reactor was

sealed and the reaction was carried out (Tab. 1). The glass reactor was heated up under stirring for 30 min at 100 °C. The obtained product was centrifuged from the mother liquor, which was then decanted off. Afterwards the product was re-dispersed and centrifuged twice in acetone and dried in air at 70 °C. Before the characterization the compounds were treated in acetone for 24 h under stirring at room temperature and dried in air at 70 °C.

Circular dichroism spectroscopy

First, 7 mg MOF was dissolved in 1 mL 50 mM NaOD solution in D₂O. The resulting suspension was centrifuged, decanted and the concentration of aspartate in the supernatant was quantified using liquid ¹H-NMR with 3-(trimethylsilyl)-2,2,3,3-tetraduteropropionic acid as external standard. The supernatant was subsequently 1:2 diluted in 50 mM NaOH to minimize interference of the Ce cations during the circular dichroism measurements. As reference, solutions of 25 mM L-,D- or LD-aspartic acid in 50 mM NaOH were prepared. The enantiomeric excess was determined by titrating the samples with a 30 mM L- or D-H₂Asp solution until a racemic mixture was obtained. The samples were kept at a constant temperature of 20 ± 0.1 °C during the recording of all spectra.

¹H-NMR spectroscopy

¹H-NMR spectroscopy was utilized to detect possible linker modification and the relative amounts of incorporated formic acid used as modulator in some reactions. Before the ¹H-NMR measurements, the title compounds were dissolved in a mixture of deuterated dimethyl sulfoxide (d₆-DMSO) and 10 % deuteriochloric acid (DCI) in D₂O (molar ratio 7:1).

SHG spectroscopy

Optical non-linear second-harmonic generation (SHG) is possible in non-centrosymmetric media only, whereas even-order susceptibilities and with it the SHG response vanishes in case of the presence of a center of inversion. As such, the analysis of SHG response helps to investigate symmetry properties of bulk material and to support the assignment of space groups, in particular in cases where unambiguous analysis of single-crystal X-ray diffraction is not possible. Although beyond the capabilities of our experimental setup, it should be noted that a full polarization and orientation dependent analysis of the SHG response of an ensemble of randomly oriented crystallites with SHG microscopy has been shown recently to allow for correct assignment of point group symmetries.^{33,34} Laser pulses with a pulse duration of 30 ps and pulse energies of up to 300 μJ/pulse at a wavelength of 1000 nm have been generated by an Optical Parametric Generator (OPG, Ekspla PG401) pumped by 9 mJ of the third-harmonic of a mode-locked Nd:YAG laser (Ekspla PL2241A) at a repetition rate of 10 Hz. A beamsplitter was used to monitor the laser pulse intensity with a photodetector (Thorlabs PDA10CF-EC). The beam was focused with an angle of incidence of about 45° onto the sample material, which was placed on a microscope slide on a height-adjustable stage. SHG response at 500 nm was monitored in reflection geometry by passing the

Figure 2. PXRD patterns ($\lambda = 1.5401 \text{ \AA}$) of the title compounds.

light through a highpass filter for suppression of fundamental radiation. Following a monochromator (Sol instruments MS2001), the SHG photons were detected by a gated photomultiplier (Hamamatsu R7899). Both fundamental and second-harmonic beam were chosen to be linearly p-polarized by means of a halfwave plate and a Glan polarizer, respectively. The signal was averaged for 5 minutes and has been corrected for background signal contributions.

Results and discussion.

Synthesis

All products with the six linker molecules were obtained as highly crystalline powders in water based synthesis, after very short reaction times (Fig. 2), the latter fact being typical for Ce-MOFs.^{4,25,35} For the syntheses of Ce-UiO-66-MS, Ce-CAU-41 and Ce-CAU-44 a large excess of linker was used, due to their high solubility in water. For the synthesis of the aspartate based UiO-66 type compounds a water to formic acid ratio of approximately 1 : 1 was necessary, due to the very low solubility of aspartic acid in pure water. All resulting products were dried and washed as previously described and fully characterized. The PXRD patterns of all title compounds are given in Figure 2.

Crystal Structures of UiO-66 type compounds

Figure 3. Color scheme: Ce and Ce-O-clusters (orange), C (grey), O (red), N (blue). Left: The inorganic building unit, a hexanuclear cluster with additional six connected water molecules $[\text{Ce}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{H}_2\text{O})_6]^{12+}$, is ideally connected by twelve carboxylates to form the three-dimensional framework structure. Strong hydrogen bonds (2.53(13) Å) are formed by six NH_2 -groups of the linker molecules to the additional connected water molecules of the hexanuclear clusters; one of these is exemplarily shown by a dotted blue line. Right: Crystal structure of Ce-UiO-66-DL-ASP viewed along the 101-axis. The occupation number of each nitrogen is 0.5.

The structures of all title compounds were determined from PXRD data; the crystallographic data are given in Table 2. The crystal structure of Ce-UiO-66-DL-ASP was refined by Rietveld

Table 2. Crystallographic data of the title compounds.

Compound	method of Refinement	space group	crystal system	lattice parameters [Å]	r_{wp} (%)	GoF	r_{Bragg} (%)
Ce-UiO-66-DL-ASP	Rietveld	$Pn\bar{3}$	cubic	$a = 18.65148(16)$	9.961	1.82 6	4.331
Ce-UiO-66-D-ASP	Le Bail	$P23$	cubic	$a = 18.6676(2)$	6.795	1.60 5	-
Ce-UiO-66-L-ASP	Le Bail	$P23$	cubic	$a = 18.6643(2)$	6.655	1.53 8	-
Ce-UiO-66-MS	Le Bail	$Pn\bar{3}$	cubic	$a = 18.6035(2)$	5.682	1.63 4	-
Ce-UiO-66-DMS	Le Bail	$Pn\bar{3}$	cubic	$a = 18.5860(5)$	8.862	2.31 2	-
Ce-CAU-41	Rietveld	$Pnnm$	orthorhombic	$a = 10.6027(3)$ $b = 12.6481(4)$ $c = 20.3238(5)$	8.957	2.58 7	3.741
Ce-CAU-44	Rietveld	$Pnnm$	orthorhombic	$a = 10.6094(3)$ $b = 12.5145(4)$ $c = 20.4034(6)$	6.817	2.04 2	3.599

methods (discussed in detail in the ESI (Chapter 1.1, Fig. S1-S2, Tab. 1). Ce-UiO-66-DL-ASP crystallizes in **fcu** topology like UiO-66,⁷ MOF-801²¹ and MIP-203.³⁶ In contrast to the inorganic building unit in the latter compounds, hexanuclear clusters with additionally coordinated water molecules of cluster composition $[Ce_6(\mu_3-O)_4(\mu_3-OH)_4(H_2O)_6]^{12+}$ are observed. The cluster is known in neptunium(IV)¹⁷ and thorium(IV)³⁷ chemistry and the similarity is due to the nearly identical ionic radii of these metals (CN = 8, Ce = 97 pm, Np = 98 pm and Th = 105 pm vs. Zr = 84 pm).³⁸ The additional water molecules are coordinating to the cerium(IV) ions, hence monocapped square antiprismatic CeO_9 polyhedra are formed (Fig. S3). Based on the donor-acceptor distances (2.53(13) Å), hydrogen bonds between the additional coordinated H_2O molecule and the NH_2 -group of the aspartate ion are anticipated (Fig. 3 and S4). These clusters are connected by twelve dicarboxylate ions (DL-ASP²⁻) to build a three-dimensional network with composition $[Ce_6(\mu_3-O)_4(\mu_3-OH)_4(H_2O)_6(D-ASP)_3(L-ASP)_3]$ (Fig. 3). Only the structure of the racemate containing MOF could be refined and an ordered arrangement of the respective D- and L-enantiomer in the framework was observed.

The incorporation of pure enantiomers or the racemic linkers (D-, L- and DL-ASP²⁻) was confirmed by circular dichroism (CD) spectroscopy after dissolution of the respective compound in NaOH. First, the two dissolved enantiomers of the pure linker were measured and opposite response signals were observed. The racemic mixture gave as expected a zero signal (Fig. S12). Thereafter the three aspartate-based MOFs were measured and the spectra display the same trend: a positive signal for Ce-UiO-66-L-ASP, a zero signal for Ce-UiO-66-DL-ASP and a negative signal for Ce-UiO-66-D-ASP. The enantiomeric excess could however not directly be related to the signal intensity because the Ce(IV) ions in solution, resulting from the MOF decomposition, strongly absorb in the UV region and severely mask the H_2ASP signal. The resulting spectra (Fig. 4) are therefore much noisier than the spectra of the pure linker (Fig. S12).

In addition, coordination of the Ce(IV) ions to the aspartate ions in solution could not be excluded, which would also influence the signal intensity. For these reasons, quantification of the enantiomer excess was performed via titration with the opposite enantiomer. Ce-UiO-66-L-ASP was titrated with one

equivalent of D-H₂ASP resulting in the complete disappearance of the signal. The same procedure was carried out for Ce-UiO-66-D-ASP. The CD spectra of the dissolved Ce-UiO-66-L-ASP and Ce-UiO-66-D-ASP before and after addition of equimolar amounts of the opposite enantiomer are shown in Figure 5. Considering the large potential error due to the dissolution and the significant noise on the measurement, this indicates that no racemization takes place during synthesis. The samples were measured a second time after 6 h to study whether partial

Table 3: Results of SHG analysis. *S* refers to the signal intensity (in arb. u.) detected at the SHG wavelength of 500 nm, *I* to the pulse intensity (in arb. u.) at the fundamental wavelength of 1000 nm.

Sample	<i>S</i> (<i>I</i> = 1)	<i>S</i> (<i>I</i> = 0.6) / <i>S</i> (<i>I</i> = 1.0)
Blank	1.7±1.3	≈1
Ce-UiO-66-DL-ASP	0.2±1.2	≈1
Ce-UiO-66-D-ASP	24.5±1.7	0.22±0.07
Ce-UiO-66-L-ASP	25.8±1.7	0.31±0.08

racemization could occur under measurement conditions. The spectra are nearly identical demonstrating that racemization does not take place during measurements (Fig. S13). These results demonstrate the persistence of the pure enantiomers D-ASP²⁻ and L-ASP²⁻ in the framework of the UiO-66 type compounds and are in line with the results of the Rietveld refinement of Ce-UiO-66-DL-ASP. The isorecticular framework structures of Ce-UiO-66-D-ASP, Ce-UiO-66-L-ASP, Ce-UiO-66-MS and Ce-UiO-66-DMC were confirmed with the Le Bail method (Fig. S8-S11), based on the crystallographic data of Ce-UiO-66-DL-ASP. These crystallographic data are also given in Table 2 and are discussed in detail in the ESI (Chapter 1.1). Inclusion of chiral linkers into MOF materials has been tested not only as platform for chiral heterogeneous catalysis³⁹ but also as a new and promising class of non-linear optical (NLO) material for practical NLO-applications by combining the high non-linear optical coefficients of the organic material with the tuneable physical properties of the inorganic framework.⁴⁰ In order to support the CD results, to verify the expected NLO properties of the material and with it to prove the absence of centrosymmetry in D- and L-ASP based MOFs, a SHG activity test has been performed. In contrast to donor-acceptor substituted conjugated systems, which are known to possess high non-linear optical coefficients^{41,42}, the SHG response of the ASP systems is expected to be comparably low. Nevertheless, we were able to observe clear SHG response for the enantiomorph structures including D-ASP²⁻ and L-ASP²⁻ as linker molecule. Table 3 summarizes the outcome of the SHG measurement. For both chiral MOFs, similar SHG signal intensities have been observed whereas the signal was close to the noise level in case of the achiral sample of the racemic Ce-UiO-66-DL-ASP material. A control experiment with the intensity of the fundamental laser pulse reduced by inserting a grey filter into the beam path confirmed the non-linear origin of the detected signal. The observed strong decrease of the SHG intensity did not follow exactly the expected square dependence of a second-order non-linear optical process, however, facing the

Figure 6. Crystal structure of Ce-CAU-41 viewed along the *b*-axis (left) and *a*-axis (right), respectively. Colour scheme on the left: Ce and Ce-O-clusters (orange), C (grey), O (red). Note that in contrast to the structure of Ce-CAU-44 bridging between the Ce-O-clusters along the *a*-axis is not taking place.

overall inaccuracies of the experimental procedure, it is fully consistent with a pure SHG response. Based on the results of CD spectroscopy and SHG measurements Ce-UiO-66-L-ASP and Ce-UiO-66-D-ASP must crystallize in a non-centrosymmetric space group. Evaluation of the PXRD data shows that the compounds crystallise in a cubic space group with lower symmetry than the one determined for Ce-UiO-66-DL-ASP (*Pn* $\bar{3}$). Hence, a LeBail fit was carried out in lowest possible space group symmetry *P*23.

Crystal Structures of CAU-41 and CAU-44

The crystal structure of Ce-CAU-41 was refined by Rietveld methods and is discussed in detail in the ESI (Chapter 1.2, Fig. S5-S6, Tab. S2). The MOF Ce-CAU-41 contains the well-known hexanuclear [Ce₆(μ₃-O)₄(μ₃-OH)₄]¹²⁺ cluster as IBU. In Ce-CAU-41 each hexanuclear cluster is connected by eight succinate molecules (SUC²⁻) in *bcu* topology (Fig. 6) as previously reported for some Zr-MOFs.^{36,43,44} The remaining coordination sites are occupied by hydroxide ions and water molecules as known from the literature^{25,27,29,45} and confirmed by ¹H-NMR spectroscopy (Fig. S22), leading to the composition [Ce₆(μ₃-O)₄(μ₃-OH)₄(SUC)₄(OH)₄(H₂O)₄].

The crystal structure of Ce-CAU-44 was refined by Rietveld methods and is also discussed in more detail in the ESI (Chapter 1.3, Fig. S7, Tab. S3). The Rietveld refinement of Ce-CAU-44 is given in Figure 7; the crystallographic data are summarized in Table 1. In CAU-44 the hexanuclear clusters are also connected

Figure 7. Rietveld refinement of Ce-CAU-44. The observed PXRD pattern ($\lambda = 1.5401$ Å) (black), the calculated curve (red) and the difference plot (blue) are shown. The allowed peak positions are marked as black ticks.

by eight succinate molecules (SUC^{2-}) in **bct** topology just like in CAU-41. Additionally, nitrate molecules (NO_3^-) are connecting the clusters to each other along the a -axis. This results in a ten-fold connected framework with **bct** topology (Fig. 8). To the best of our knowledge CAU-44 is the first Ce(IV)-based MOF

where the hexanuclear clusters are connected by nitrate ligands, but such molecular complexes with nitrate ions as ligands are known.⁴⁶ The remaining coordination sites are occupied by hydroxide ions and water molecules, which was

Table 4. Summarized results of some of the characterization of the title compounds. The whole characterization is given in detail in the ESI.

Compound	N ₂ sorption [m ² g ⁻¹]	H ₂ O sorption [wt%]	Thermal decomposition [°C]	Determined connectivity	Theoretical connectivity	CHN results [%]	CHN theoretical [%]
Ce-UiO-66-DL-ASP	-	8.77	225(5)	11.2-c	12-c	C: 12.63 H: 3.14 N: 4.09	C: 12.84 H: 3.95 N: 3.74
Ce-UiO-66-D-ASP	-	8.77	225(5)	11.2-c	12-c	C: 12.72 H: 3.32 N: 4.02	C: 12.84 H: 3.95 N: 3.74
Ce-UiO-66-L-ASP	-	14.85	225(5)	11.2-c	12-c	C: 12.69 H: 3.41 N: 3.99	C: 12.84 H: 3.95 N: 3.74
Ce-UiO-66-MS	173	14.85	220(5)	11.2-c	12-c	C: 14.68 H: 2.41 N: 0.10	C: 16.22 H: 4.23 N: 0.00
Ce-UiO-66-DMS	-	8.11	155(5)	11.2-c	12-c	C: 21.21 H: 3.57 N: 0.19	C: 21.81 H: 4.04 N: 0.00
Ce-CAU-41	-	6.85	220(5)	8-c	8-c	C: 13.26 H: 2.77 N: 0.02	C: 13.46 H: 3.80 N: 0.00
Ce-CAU-44	-	8.44	210(5)	10-c	10-c	C: 14.98 H: 2.84 N: 1.57	C: 14.47 H: 3.59 N: 1.35

Figure 8. Crystal structure of Ce-CAU-44 viewing along the b -axis (top) and a -axis (bottom), respectively. Colour scheme on the left: Ce and Ce-O-clusters (orange), C (grey), O (red), N (blue). Note that in contrast to the structure of Ce-CAU-41 bridging between the Ce-O-clusters along the a -axis is taking place.

confirmed by $^1\text{H-NMR}$ spectroscopy (Fig. S23). Summarizing, $[\text{Ce}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{SUC})_4(\text{NO}_3)_2(\text{OH})_2(\text{H}_2\text{O})_2]$ adequately describes the composition.

Thermogravimetric analysis

Thermogravimetric analyses (TGA) were carried out to confirm the composition and phase purity of the previously described compounds. Therefore, each sample was heated up to 800 °C under an air stream and the mass losses were detected (Figs. S14-S18). In the first step, for each of the observed two step decomposition processes, physisorbed water molecules and small amounts of solvent residues were removed from the sample. These mass losses range between 9.4 and 21.4 wt %. In the second step, the framework decomposition of all title compounds takes place. These mass losses agree well with the theoretical values for the decomposition steps and the results are summarized in Table S4. Only minor differences between the theoretical and measured values are observed, which can be explained by the presence of minor linker defects in UiO-66 type compounds as often observed for Zr- and Ce-MOFs (Tab. 3).^{11,47,48} The remaining coordination sites are occupied by hydroxide ions and water molecules as described in the literature^{4,25,35} and verified by $^1\text{H-NMR}$ spectroscopy (Fig. S19-S21). The thermal decomposition products were postulated to

consist of CeO₂, as previously reported for the thermal decomposition of Ce(IV)-MOFs in the literature.^{4,25,27,35}

Spectroscopy

¹H-NMR spectroscopy was used to confirm the incorporation of the different linker molecules. In addition, formic acid was used as a modulator in the synthesis of some of the title compounds. As a modulator, formic acid can affect the connectivity and therefore also the topology of the resulting MOFs as previously described in the literature.⁴⁹ If the hexanuclear clusters are not fully connected by linker molecules, the remaining coordination sites will be occupied by counterions, i.e. HCOO⁻, AcO⁻ or OH⁻/Cl⁻ ions and water molecules.^{4,21,49} Therefore, we measured a series of ¹H-NMR spectra (Figs. S19–S23) and determined the proton ratios of the linker and modulators by integration of the proton signals. For all UiO-66 type compounds only minor amounts of formic acid were detected. For Ce-CAU-41 only minor amounts of HCOOH were detected as well (SUC²⁻ : HCOO⁻ = 4.00 : 0.17, Fig. S22). Hence we expect that the remaining coordination sites at the hexanuclear cluster are nearly exclusively occupied by hydroxide ions and water molecules. In the ¹H-NMR spectrum of Ce-CAU-44 only the signals corresponding to the linker molecules (SUC²⁻) were observed (Fig. S23). All of these measurements are confirmed by elemental analysis (Tab. 3). The IR spectra of the title compounds are shown in Figure. S24 and assigned in Table S5–S6. Furthermore, the IR spectra are consistent with the prior characterization as no other organic molecules were detected. Thus the compositions are confirmed.

Thermal and chemical stability

The thermal stabilities were determined by thermogravimetric (TG) analysis. Ce-UiO-66-ASP shows the highest thermal stability and decomposes under an air stream at 225 °C. For the other investigated compounds, the thermal stability is slightly lower (Tab. 3). The chemical stability of each title compound was investigated by stirring for 24 h in several organic solvents, acidic (2 M HCl) and basic (2 M NaOH) aqueous solutions. Thereafter the stabilities were investigated by PXRD. Generally, the materials have a fair to excellent stability to water and many organic solvents; the UiO-66 materials are more stable (asp > MS, DMS), while Ce-CAU-44 is significantly less stable and even displays structure loss in water or in DMSO. Also acetic acid causes damage to many of the here described Ce MOFs (Fig. S25–S29) and summarized in Table S7.

Sorption.

N₂ sorption measurements were performed to assess the porosity of the title compounds (Fig. S30, Tab. 3 and S8). Ce-UiO-66-MS (**fcu** topology) exhibits a specific BET surface area of 173 m² g⁻¹. The other UiO-66 analogues in **fcu** topology showed no nitrogen uptake. This observation can be explained by the larger steric demand of DMS²⁻ and the strongly hygroscopic properties of the ASP²⁻ which also lead to an increase in the coordination Ce(IV) coordination number from 8 to 9. The smallest linker used in the study, i.e. H₂SUC leads to the formation of Ce-CAU-41 (**bcu** topology) and Ce-CAU-44 (**bct** topology). In these structures, short distances between Ce-O-

clusters along the *a*-axis are observed which limits the porosity. Thus these compounds showed no N₂ uptake after the identical sample treatment. H₂O sorption measurements of the title compounds show only small amounts of water uptake (Fig. S32–S33, Tab. 3 and S9). After each sorption measurement the stability of the compounds was confirmed and by PXRD measurements (Fig. S31 and S34).

Conclusion.

In our contribution, we have shown an easy way for MOF synthesis using a series of chiral and achiral dicarboxylic C₄-acids to obtain Ce(IV)-MOFs. In water-based syntheses under mild reaction conditions, six compound crystallizing in different topologies **fcu**, **bcu** and **bct**, were obtained within 30 min. In the UiO-66 type structures hexanuclear clusters with additional coordinating water molecules ([Ce₆(μ₃-O)₄(μ₃-OH)₄(H₂O)₆]¹²⁺) are observed which are hitherto unknown in Ce(IV) chemistry. The Rietveld method was used to determine the structure of Ce-UiO-66-DL-ASP and ordering of D- and L-ASP²⁻ ions was observed. Circular dichroism spectroscopy and SHG-measurements were employed, to demonstrate that the racemic mixture as well as the pure D- and L-enantiomers can be incorporated into the framework. With 2-methylsuccinic acid (H₂MS) and 2,3-dimethylsuccinic acid (H₂DMS) isorecticular compounds were obtained.

The corresponding unfunctionalized aliphatic linker succinic acid leads to the formation of two Ce(IV)-MOFs denoted as Ce-CAU-41 and Ce-CAU-44, and both contain the IBU [Ce₆(μ₃-O)₄(μ₃-OH)₄]¹²⁺. In both structures the IBUs are eightfold connected by succinate ions. In Ce-CAU-44 an additional interconnection by nitrate ligands is observed which results in a framework with **bct** topology. This work shows the diversity for Ce(IV)-MOFs that can be obtained, when aliphatic saturated dicarboxylic acids are used as the linker. Future investigations will focus on the study of the Ce(IV)-MOFs containing chiral linker molecules in chiral catalysis.

Conflicts of interest.

There are no conflicts to declare.

CCDC Numbers.

Ce-CAU-41:	CCDC 1909174
Ce-UiO-66-DL-ASP:	CCDC 1909175
Ce-CAU-44:	CCDC 1909176

Acknowledgment.

The authors thank Jens Moons and Prof. Dr. Tatjana Vogt for their help with the CD measurements. GF and FL thank the Cluster of Excellence “Future Ocean” (DFG - EC80) at Kiel University for funding the SHG setup and support through the HOSST (Helmholtz Research School Ocean Science and

Technology) program at GEOMAR. Initial setup and characterization of the SHG setup by Kristian Laß and Anna Reese is gratefully acknowledged.

Notes and references

- O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705–714.
- N. Stock and S. Biswas, *Chem. Rev.*, 2012, **112**, 933–969.
- G. Férey, *Chem Soc Rev*, 2008, **37**, 191–214.
- M. Lammert, M. T. Wharmby, S. Smolders, B. Bueken, A. Lieb, K. A. Lomachenko, D. D. Vos and N. Stock, *Chem. Commun.*, 2015, **51**, 12578–12581.
- D. Lenzen, P. Bendix, H. Reinsch, D. Fröhlich, H. Kummer, M. Möllers, P. P. C. Hügenell, R. Gläser, S. Henninger and N. Stock, *Adv. Mater.*, 2018, **30**, 1705869.
- S. H. Jhung, N. A. Khan and Z. Hasan, *CrystEngComm*, 2012, **14**, 7099.
- J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850–13851.
- Y. Bai, Y. Dou, L.-H. Xie, W. Rutledge, J.-R. Li and H.-C. Zhou, *Chem. Soc. Rev.*, 2016, **45**, 2327–2367.
- L. Valenzano, B. Civalieri, S. Chavan, S. Bordiga, M. H. Nilsen, S. Jakobsen, K. P. Lillerud and C. Lamberti, *Chem. Mater.*, 2011, **23**, 1700–1718.
- M. J. Katz, Z. J. Brown, Y. J. Colón, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp and O. K. Farha, *Chem. Commun.*, 2013, **49**, 9449.
- G. C. Shearer, S. Chavan, J. Ethiraj, J. G. Vitillo, S. Svelle, U. Olsbye, C. Lamberti, S. Bordiga and K. P. Lillerud, *Chem. Mater.*, 2014, **26**, 4068–4071.
- J. B. DeCoste, G. W. Peterson, H. Jasuja, T. G. Glover, Y. Huang and K. S. Walton, *J. Mater. Chem. A*, 2013, **1**, 5642.
- J. Jacobsen, J. Gosch and N. Stock, *Z. Für Anorg. Allg. Chem.*, 2018, **644**, 1771–1776.
- S. Jakobsen, D. Gianolio, D. S. Wragg, M. H. Nilsen, H. Emerich, S. Bordiga, C. Lamberti, U. Olsbye, M. Tilset and K. P. Lillerud, *Phys. Rev. B*, 2012, **86**, 125429.
- C. Falaise, C. Volkringer, J.-F. Vigier, N. Henry, A. Beaurain and T. Loiseau, *Chem. - Eur. J.*, 2013, **19**, 5324–5331.
- C. Falaise, J.-S. Charles, C. Volkringer and T. Loiseau, *Inorg. Chem.*, 2015, **54**, 2235–2242.
- N. P. Martin, J. März, H. Feuchter, S. Duval, P. Roussel, N. Henry, A. Ikeda-Ohno, T. Loiseau and C. Volkringer, *Chem. Commun.*, 2018, **54**, 6979–6982.
- M. Kandiah, M. H. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E. A. Quadrelli, F. Bonino and K. P. Lillerud, *Chem. Mater.*, 2010, **22**, 6632–6640.
- S. Biswas, J. Zhang, Z. Li, Y.-Y. Liu, M. Grzywa, L. Sun, D. Volkmer and P. Van Der Voort, *Dalton Trans.*, 2013, **42**, 4730.
- G. Wißmann, A. Schaate, S. Lilienthal, I. Bremer, A. M. Schneider and P. Behrens, *Microporous Mesoporous Mater.*, 2012, **152**, 64–70.
- H. Furukawa, F. Gándara, Y.-B. Zhang, J. Jiang, W. L. Queen, M. R. Hudson and O. M. Yaghi, *J. Am. Chem. Soc.*, 2014, **136**, 4369–4381.
- S. Smolders, K. A. Lomachenko, B. Bueken, A. Struyf, A. L. Bugaev, C. Atzori, N. Stock, C. Lamberti, M. B. J. Roefsaers and D. E. De Vos, *ChemPhysChem*, 2018, **19**, 373–378.
- T. Islamoglu, A. Atilgan, S.-Y. Moon, G. W. Peterson, J. B. DeCoste, M. Hall, J. T. Hupp and O. K. Farha, *Chem. Mater.*, 2017, **29**, 2672–2675.
- C. Zhu, T. Ding, W. Gao, K. Ma, Y. Tian and X. Li, *Int. J. Hydrog. Energy*, 2017, **42**, 17457–17465.
- M. Lammert, C. Glißmann, H. Reinsch and N. Stock, *Cryst. Growth Des.*, 2017, **17**, 1125–1131.
- S. Smolders, A. Struyf, H. Reinsch, B. Bueken, T. Rhauderwiek, L. Mintrop, P. Kurz, N. Stock and D. E. De Vos, *Chem. Commun.*, 2018, **54**, 876–879.
- M. Lammert, H. Reinsch, C. A. Murray, M. T. Wharmby, H. Terraschke and N. Stock, *Dalton Trans.*, 2016, **45**, 18822–18826.
- S. Waitschat, D. Fröhlich, H. Reinsch, H. Terraschke, K. A. Lomachenko, C. Lamberti, H. Kummer, T. Helling, M. Baumgartner, S. Henninger and N. Stock, *Dalton Trans.*, 2018, **47**, 1062–1070.
- R. D'Amato, A. Donnadio, M. Carta, C. Sangregorio, D. Tiana, R. Vivani, M. Taddei and F. Costantino, *ACS Sustain. Chem. Eng.*, 2019, **7**, 394–402.
- S. Bauer and N. Stock, *Chem. Unserer Zeit*, 2007, **41**, 390–398.
- N. Stock, *Chem. Ing. Tech.*, 2010, **82**, 1039–1047.
- F. Rouquerol, J. Rouquerol, K. S. W. Sing, P. L. Llewellyn and G. Maurin, *Adsorption by powders and porous solids: principles, methodology and applications*, Elsevier/AP, Amsterdam, Second edition., 2014.
- M. A. van der Veen, F. Vermoortele, D. E. De Vos and T. Verbiest, *Anal. Chem.*, 2012, **84**, 6378–6385.
- M. A. van der Veen, F. Vermoortele, D. E. De Vos and T. Verbiest, *Anal. Chem.*, 2012, **84**, 6386–6390.
- J. Jacobsen, H. Reinsch and N. Stock, *Inorg. Chem.*, 2018, **57**, 12820–12826.
- M. Wahiduzzaman, S. Wang, B. J. Sikora, C. Serre and G. Maurin, *Chem. Commun.*, 2018, **54**, 10812–10815.
- J. Lin, G. B. Jin and L. Soderholm, *Inorg. Chem.*, 2016, **55**, 10098–10101.
- R. D. Shannon, *Acta Crystallogr. Sect. A*, 1976, **32**, 751–767.
- G. Nickerl, A. Henschel, R. Grunker, K. Gedrich and S. Kaskel, *Chem. Ing. Tech.*, 2011, **83**, 90–103.
- S. Du and H. Zhang, in *Metal-Organic Frameworks for Photonics Applications*, Springer, 2013, pp. 145–165.
- J. Zyss and D. Chemla, in *Nonlinear optical properties of organic molecules and crystals*, Elsevier, 1987, pp. 23–191.
- D. S. Chemla, *Nonlinear optical properties of organic molecules and crystals*, Elsevier, 2012, vol. 1.
- H. Reinsch, B. Bueken, F. Vermoortele, I. Stassen, A. Lieb, K.-P. Lillerud and D. De Vos, *CrystEngComm*, 2015, **17**, 4070–4074.
- H. Reinsch, I. Stassen, B. Bueken, A. Lieb, R. Ameloot and D. De Vos, *CrystEngComm*, 2015, **17**, 331–337.
- A. C. Dreischarf, M. Lammert, N. Stock and H. Reinsch, *Inorg. Chem.*, 2017, **56**, 2270–2277.
- R. Das, R. Sarma and J. B. Baruah, *Inorg. Chem. Commun.*, 2010, **13**, 793–795.
- H. Wu, Y. S. Chua, V. Krungleviciute, M. Tyagi, P. Chen, T. Yildirim and W. Zhou, *J. Am. Chem. Soc.*, 2013, **135**, 10525–10532.
- P. Ghosh, Y. J. Colón and R. Q. Snurr, *Chem Commun*, 2014, **50**, 11329–11331.
- V. Bon, I. Senkovska, I. A. Baburin and S. Kaskel, *Cryst. Growth Des.*, 2013, **13**, 1231–1237.