A precursor method for the synthesis of new Ce(IV) MOFs with reactive tetracarboxylate linkers[†]

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A precursor method has been developed to synthesize Ce(IV) MOFs that could not be prepared directly from Ce(IV) salts. Starting from Ce₆ clusters, two Ce-UiO-66 analogues and four tetracarboxylate-based Ce(IV) MOFs could be synthesized. The applied method facilitates framework formation by evading reactive individual Ce(IV)-ions thereby paving the way for further development of Ce-MOFs.

Metal-organic frameworks (MOFs) are crystalline, potentially porous materials built up from metal cations and organic linkers. They can be easily adjusted by varying both organic linker and metal ion and are thus highly tunable in pore size and chemical functionality. This renders them suitable candidates for gas separation, gas adsorption and catalysis, among other applications.^{1–4} One of the most studied MOFs is UiO-66 [Zr₆O₄(OH)₄(BDC)₆] (BDC = 1,4-benzenedicarboxylate), a highly stable MOF constructed of 12-fold connected hexanuclear [Zr₆O₄(OH)₄]¹²⁺ clusters (UiO = University of Oslo).⁵ In recent years, numerous Zr-MOFs featuring the same hexanuclear cluster but exhibiting a variety of different topologies have been reported. Typically, the Zr₆ clusters are connected by 6 to 12 di-, tri- or tetracarboxylate linkers, whereby the excess positive charge of the cluster is further balanced by hydroxy/methoxy groups or by modulators such as formate or benzoate ions.^{6,7} A broad variety of Zr₆-MOFs based on tetracarboxylate linkers has been reported because these linkers, such as tetrakis(*p*-carboxylatophenyl)porphyrin (H₂TCP⁴⁻), can imbue the resulting MOFs with (photo)catalytic or sensing properties.^{8–21}

Besides expanding the number of MOF structures available for a single metal cation, a single framework can often be synthesized with several different cations. UiO-66 has for instance already been synthesized with Hf(IV), U(IV), Th(IV) and Ce(IV).^{22–25} The latter was shown to be redox active and its catalytic activity was confirmed in the aerobic oxidation of benzyl alcohol.^{25,26} Since the discovery of Ce-UiO-66, a series of new Ce(IV)-MOFs including four other topologies has been reported with only minor changes in the synthesis procedure relative to Ce-UiO-66.^{17,27,28} Further development of Ce(IV)-based MOFs is however difficult because Ce(IV) is a strong oxidant (Ce(III)/Ce(IV): 1.61 V vs. SHE) and tends to get reduced during synthesis. This is for instance the case for the MOFs designated as CAU-18 and CAU-19 (CAU = Christian Albrechts University) which are synthesized from cerium(IV) ammonium nitrate (CAN) and H₂TCP⁴⁻, but feature nodes containing exclusively Ce(III).²⁹ Undesired precursor side-reactions can however be circumvented by employing pre-formed molecular clusters which would normally be formed during synthesis, rather than simple metal salts. These clusters are considered to exchange their capping ligands for linker molecules during synthesis to form a 3D framework. Methacrylate-capped hexanuclear Zr₆ clusters were used in an early example of this precursor approach to prepare UiO-66-Muc (Muc²⁻ = *trans,trans*-muconate), which could not be synthesized directly from simple Zr salts.³⁰ Hexanuclear Ce₆ clusters related to those found in Ce(IV)-MOFs have already been repeatedly reported, even as early as in 1956, but have not been used in a similar fashion as inorganic building units for MOF synthesis.³¹ The first reported molecular [Ce₆O₄(OH)₄]¹²⁺ cluster features charge compensation by 6 coordinated sulfate ions; however more recent synthetic procedures allow to obtain clusters with the same Ce₆ core but ligated by organic acetylacetonate or carboxylate ligands.^{32–36}

Herein, a new precursor method starting from a known glycinate/nitrate coordinated cerium cluster [Ce₆O₄(OH)₄(NH₃CH₂COO)₈(NO₃)₄(H₂O)₆Cl₈·8H₂O] is developed to synthesize Ce(IV)-MOFs featuring tetracarboxylate linkers

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such as 1,3,6,8-tetrakis(*p*-benzoate)pyrene (TBAPy⁴⁻) and H₂TCPP⁴⁻, for which direct synthesis from Ce(IV) salts proved unsuccessful (Fig. 1).³⁶ This precursor method was first applied to form the known Ce-UiO-66, Ce-UiO-66-Fum (Fum²⁻ = fumarate), Ce-UiO-66-NDC (NDC²⁻ = 2,6-naphthalenedicarboxylate) and Ce-UiO-67 frameworks. Subsequently, six new Ce(IV)-MOFs comprising two aliphatic dicarboxylate MOFs (Ce-UiO-66-Muc [Ce₆(OH)₄O₄(Muc)₆] and Ce-UiO-66-CDC (CDC²⁻ = *trans*-1,4-cyclohexanedicarboxylate) [Ce₆(OH)₄O₄(CDC)₆]) and four tetracarboxylate-based MOFs (Ce-PCN-224(Zn) [Ce₆(OH)₄O₄(BA)₆(TCPP-Zn)_{1.5}] (BA⁻ = benzoate), Ce-MOF-545(Sn) [Ce₆(OH)₄O₄(BA)₄(TCPP-SnCl₂)₂], Ce-NU-1000 [Ce₆(OH)₄O₄(BA)₄(TBAPy)₂] and Ce-CAU-24-TBAPy [Ce₆(OH)₄O₄(BA)₄(TBAPy)₂]) were synthesized.

All compounds were obtained starting from dissolved linker and modulator mixed with an aqueous solution of preformed Ce₆ clusters (details in ESI). The glycinate/nitrate-capped precursor cluster could be easily synthesized in water at room temperature and its synthesis was successfully scaled up to obtain 20 g clusters per batch (Fig. S1). All MOF structures were verified *via* powder X-ray diffraction (PXRD) of a solvent-filled sample.

Cluster-based synthesis of Ce-UiO-66, Ce-UiO-66-Fum, Ce-UiO-66-NDC and Ce-UiO-67 resulted in materials with good crystallinity. The new Ce-UiO-66-Muc is also highly crystalline and displays a BET surface area of 966 m²/g, slightly higher than Ce-UiO-66 synthesized in this work (*S*_{BET} = 884 m²/g). Ce-UiO-66-CDC is swollen in DMF and highly crystalline but it is not porous after evacuation, in analogy with Zr-UiO-66-CDC (Fig. S2-S5).³⁷

The PXRD pattern of Ce-PCN-224(Zn) resembles well that of PCN-224; it was therefore Le Bail fitted in space group *Im* $\bar{3}$ *m* to extract the unit cell dimensions (Fig. S6 and S7, Table S1).¹⁴ A model was built starting from PCN-224 in which all Zr atoms were replaced by Ce and the unit cell was imposed to adopt the

cell parameters extracted by the Le Bail refinement. Due to the large number of disordered electrons associated with adsorbed guests in the pores of the material and the structural collapse upon removal of these guests, Rietveld refinement of the aforementioned model was not undertaken.³⁸ The obtained structure features the **she** topology. The material is built up by 6-fold TCPP-Zn⁴⁺ connected [Ce₆(μ₃-OH)₄(μ₃-O)₄]¹²⁺ clusters with six capping benzoate ions each and contains square-shaped channels of 20 Å diameter. The determined metal content (Ce: 27.3%; Zn: 3.2%) is in excellent agreement with the theoretical values (Ce: 28.1%; Zn: 3.3%) and confirms the persisting metalation of the linker. Liquid ¹H NMR spectroscopy of the digested sample yielded a HBA:H₄TCPP-Zn ratio of 8.31, which is higher than the theoretical value (HBA:H₄TCPP-Zn = 6), likely due to residual modulator in the solvent-filled pores. Ce-PCN-224 could also be synthesized starting from metal-free H₆TCPP or H₄TCPP-SnCl₂ (Fig. S8).

The PXRD pattern of Ce-MOF-545(Sn) resembles well that of MOF-545 and was therefore Le Bail fitted in space group *P6/mmm*. Additional reflections present in the PXRD pattern were attributed to traces of Ce-MOF-525(Sn).¹⁶ Due to the high quality synchrotron data, the structure could be reasonably well modeled using Rietveld methods starting from a Ce-substituted and relaxed MOF-545 structure with an additional Ce-MOF-525(Sn) phase as by-product (Fig. 2, Table S1, details in ESI). Ce-MOF-545(Sn) is built up from 8-fold TCPP-SnCl₂⁴⁻ connected [Ce₆(μ₃-OH)₄(μ₃-O)₄]¹²⁺ clusters with four capping benzoate ions each, featuring the **csq** topology with hexagonal mesoporous channels of 35 Å diameter and triangular microporous ones in the size of 8 Å. The metal content (Ce: 25.8%; Sn: 5.1%) is in good agreement with the expected values (Ce: 24.6%; Sn: 6.9%) although a slight deficit of Sn indicates partial Sn²⁺ leaching. The HBA:H₄TCPP-SnCl₂ ratio (2.54) confirms the presence of four benzoates per cluster. Remarkably, Ce-MOF-545 could only be

Fig. 1 Preformed hexanuclear Ce₆ cluster and tetracarboxylate linkers as building blocks for the synthesis of Ce-PCN-224, Ce-MOF-545, Ce-CAU-24-TBAPy and Ce-NU-1000.

synthesized using a tin metalated linker and not with a metal-free H₆TCP or Zn/Co metalated linker.

Fig. 2 Rietveld plot of Ce-MOF-545(Sn) ($\lambda = 0.412628 \text{ \AA}$). Vertical bars mark the allowed reflection positions.

Ce-NU-1000 is an isorecticular analogue of Ce-MOF-545, featuring the same **csq** topology with 8-fold connected clusters capped by four benzoate ions. Its PXRD pattern resembles that of NU-1000 and could be Le Bail fitted in space group *P6/mmm* (Fig. S9 and S10, Table S1).⁹ Its Ce content (30.8%) is in perfect agreement with the theoretical value (30.9%). Similar to Ce-PCN-224(Zn), a model was built starting from its Zr-analogue. The material has mesoporous channels of 32 Å and microporous ones of 12 Å.

The PXRD pattern of Ce-CAU-24-TBAPy resembles that of Ce-CAU-24 and was Le Bail fitted in space group *Cmmm* (Fig. S11 and S12, Table S1). A model was based on Ce-CAU-24 by replacing the original linker (tetrakis(*p*-benzoate)benzene) by TBAPy⁴, adding four capping ligands and adapting lattice parameters.¹⁷ The HBA:H₄TBAPy ratio (2.68) is slightly higher than the theoretical value (HBA:H₄TBAPy = 2), likely due to residual molecules in the pores. The latter was confirmed by a remarkably lower Ce content (25.5% vs. 30.8% (theoretical value)). The environment around the cluster is identical as in Ce-NU-1000 but the material features the **scu** topology with rhombic channels of 16 x 25 Å.

The key issue during synthesis is the stability of the linker. When Ce-NU-1000 or Ce-CAU-24-TBAPy are synthesized from CAN, a crystalline material is formed but ¹H NMR of the digested sample clearly shows that the linker is not fully preserved (Fig. 3). The characteristic peaks of H₄TBAPy are still visible but many other peaks of presumably aromatic oxidation products appear in the spectrum. This linker stability issue could only be solved by replacing CAN by preformed Ce(IV) clusters in the synthesis mixture, which resulted in a fully preserved linker under identical synthesis conditions, while no residual glycinate originating from the cluster was detected (Fig. S14). The higher stability of H₄TBAPy during synthesis with Ce₆ clusters is

rationalized by the lower reduction potential of the precursor. Estes *et al* measured a reduction potential of 0.82V vs. SHE for the cluster *via* cyclic voltammetry, which is significantly lower than 1.61V for free Ce(IV) ions.³⁶ Similarly, Ce-MOF-545 and Ce-PCN-224 could not be synthesized directly from CAN and only Ce(III) MOFs, such as CAU-19, were obtained.²⁹ Replacing CAN by Ce₆ clusters again yielded Ce(IV)-MOFs with fully preserved linkers (Fig. S15). Remarkably, prolonged synthesis time still resulted in the formation of CAU-19, similar to when CAN was used (Fig. S13). This could be due to the slow release of individual Ce(IV) ions from the cluster to form CAU-19.

The chemical and thermal stability of Ce-MOFs is generally decreased compared to their Zr isostructures due to the aforementioned redox activity and the softer character of the large Ce(IV) cation which results in weaker Ce-carboxylate bonds.^{17,25,27,39} All herein described MOFs are stable in acetone but Ce-CAU-24-TBAPy and Ce-PCN-224 significantly lose crystallinity after extensive washing with DMF. The lower stability of the former is rationalized by the rhombic pores which are more susceptible to collapse while Ce-PCN-224 is more labile due to its lower cluster connectivity. Ce-PCN-224 is however stable in a BA:DMF (20wt% BA) mixture which demonstrates that framework decomposition likely originates from BA removal (Fig. S17). In addition, Ce-PCN-224 retains its structural integrity in water:DMF (20wt% water) or decane, both with lower BA solubility than DMF. Thermal stability was investigated via TGA and decomposition occurs at approximately 350°C (Fig. S18). However, PXRD data of thermally treated samples indicates that the framework collapses at much lower temperature due to capillary forces on the large linkers, as was also reported for Ce-UiO-67.^{25,40} Only Ce-MOF-545 is moderately stable upon evacuation, its BET surface area (713 m²/g) is significantly lower than for MOF-545 (2260 m²/g) due to partial framework collapse, but its DFT calculated micro- and mesopore sizes (9 Å and 35 Å) are still in good agreement with the crystallographically determined structural model (Fig. S19).¹⁶ The redox activity of Ce-MOF-545 was demonstrated using the TEMPO-mediated aerobic

oxidation of benzyl alcohol to benzaldehyde as a test reaction, reaching a turnover number of 6 after 7 hours.

Fig. 3 Liquid ¹H NMR spectra of digested Ce-NU-1000 synthesized from CAN (top) and from clusters (bottom).

In conclusion, two new Ce-UiO-66 analogues and four new Ce(IV)-MOFs with reactive tetracarboxylate linkers were synthesized using hexanuclear Ce₆ clusters as precursors. This method circumvents reactivity issues of the previously used Ce(IV) salts which led to decomposed linkers or reduced metal nodes. The wide applicability of the procedure was demonstrated by the synthesis of materials isorecticular to a variety of Zr-MOFs. The herein reported precursor method paves the way for further development of Ce-MOFs which are especially interesting for redox catalysis.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- J. R. Li, J. Sculley and H. C. Zhou, *Chem. Rev.*, 2012, **112**, 869–932.
- H. Kim, S. Yang, S. R. Rao, S. Narayanan, E. A. Kapustin, H. Furukawa, A. S. Umans, O. M. Yaghi and E. N. Wang, *Science* (80-.), 2017, **356**, 430–434.
- J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang and C.-Y. Su, *Chem. Soc. Rev.*, 2014, **43**, 6011–6061.
- P. Horcajada, C. Serre, M. Vallet-Regí, M. Sebban, F. Taulelle and G. Férey, *Angew. Chemie - Int. Ed.*, 2006, **45**, 5974–5978.
- 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.
- 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.
- Y. Bai, Y. Dou, L.-H. Xie, W. Rutledge, J.-R. Li and H.-C. Zhou, *Chem. Soc. Rev.*, 2016, **45**, 2327–2367.
- P. Deria, D. A. Gomez-Gualdrón, I. Hod, R. Q. Snurr, J. T. Hupp and O. K. Farha, *J. Am. Chem. Soc.*, 2016, **138**, 14449–14457.
- J. E. Mondloch, W. Bury, D. Fairen-Jimenez, S. Kwon, E. J. Demarco, M. H. Weston, A. A. Sarjeant, S. T. Nguyen, P. C. Stair, R. Q. Snurr, O. K. Farha and J. T. Hupp, *J. Am. Chem. Soc.*, 2013, **135**, 10294–10297.
- O. V. Gutov, W. Bury, D. A. Gomez-Gualdrón, V. Krungleviciute, D. Fairen-Jimenez, J. E. Mondloch, A. A. Sarjeant, S. S. Al-Juaid, R. Q. Snurr, J. T. Hupp, T. Yildirim and O. K. Farha, *Chem. - A Eur. J.*, 2014, **20**, 12389–12393.
- T. C. Wang, W. Bury, D. A. Gómez-Gualdrón, N. A. Vermeulen, J. E. Mondloch, P. Deria, K. Zhang, P. Z. Moghadam, A. A. Sarjeant, R. Q. Snurr, J. F. Stoddart, J. T. Hupp and O. K. Farha, *J. Am. Chem. Soc.*, 2015, **137**, 3585–3591.
- D. Feng, Z. Y. Gu, J. R. Li, H. L. Jiang, Z. Wei and H. C. Zhou, *Angew. Chemie - Int. Ed.*, 2012, **51**, 10307–10310.
- D. Feng, Z.-Y. Gu, Y.-P. Chen, J. Park, Z. Wei, Y. Sun, M. Bosch, S. Yuan and H.-C. Zhou, *J. Am. Chem. Soc.*, 2014, **136**, 17714–17717.
- D. Feng, W. Chung, Z. Wei, Z. Gu and H. Jiang, *J. Am. Chem. Soc.*, 2013, **135**, 17105–17110.
- H. L. Jiang, D. Feng, K. Wang, Z. Y. Gu, Z. Wei, Y. P. Chen and H. C. Zhou, *J. Am. Chem. Soc.*, 2013, **135**, 13934–13938.
- W. Morris, B. Voloskiy, S. Demir, F. Gándara, P. L. McGrier, H. Furukawa, D. Cascio, J. F. Stoddart and O. M. Yaghi, *Inorg. Chem.*, 2012, **51**, 6443–6445.
- M. Lammert, H. Reinsch, C. A. Murray, M. T. Wharmby, H. Terraschke and N. Stock, *Dalt. Trans.*, 2016, **45**, 18822–18826.
- A. Fateeva, P. A. Chater, C. P. Ireland, A. A. Tahir, Y. Z. Khimyak, P. V. Wiper, J. R. Darwent and M. J. Rosseinsky, *Angew. Chemie - Int. Ed.*, 2012, **51**, 7440–7444.
- H. Q. Xu, J. Hu, D. Wang, Z. Li, Q. Zhang, Y. Luo, S. H. Yu and H. L. Jiang, *J. Am. Chem. Soc.*, 2015, **137**, 13440–13443.
- Y. Z. Chen, Z. U. Wang, H. Wang, J. Lu, S. H. Yu and H. L. Jiang, *J. Am. Chem. Soc.*, 2017, **139**, 2035–2044.
- C. W. Kung, T. H. Chang, L. Y. Chou, J. T. Hupp, O. K. Farha and K. C. Ho, *Electrochem. commun.*, 2015, **58**, 51–56.
- 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 - Condens. Matter Mater. Phys.*, 2012, **86**, 125429.
- C. Falaise, C. Volkringer, J. F. Vigier, N. Henry, A. Beaurain and T. Loiseau, *Chem. - A Eur. J.*, 2013, **19**, 5324–5331.
- C. Falaise, J. S. Charles, C. Volkringer and T. Loiseau, *Inorg. Chem.*, 2015, **54**, 2235–2242.
- M. Lammert, M. T. Wharmby, S. Smolders, B. Bueken, A. Lieb, K. A. Lomachenko, D. De Vos and N. Stock, *Chem. Commun.*, 2015, **51**, 12578–12581.
- S. Smolders, K. A. Lomachenko, B. Bueken, A. Struyf, A. L. Bugaev, C. Atzori, N. Stock, C. Lamberti, M. B. J. Roeffaers and D. De Vos, *ChemPhysChem*, DOI:10.1002/cphc.201700967.
- M. Lammert, C. Glißmann, H. Reinsch and N. Stock, *Cryst. Growth Des.*, 2017, **17**, 1125–1131.
- A. C. Dreischarf, M. Lammert, N. Stock and H. Reinsch, *Inorg. Chem.*, 2017, **56**, 2270–2277.
- T. Rhauderwiek, N. Heidenreich, H. Reinsch, S. Øien-Ødegaard, K. A. Lomachenko, U. Rütt, A. V. Soldatov, K. P. Lillerud and N. Stock, *Cryst. Growth Des.*, 2017, acs.cgd.7b00450.
- V. Guillermin, S. Gross, C. Serre, T. Devic, M. Bauer and G. Férey, *Chem. Commun.*, 2010, **46**, 767–769.
- G. Lundgren, *Recueil*, 1956, **75**, 585.
- Toledano, Ribot and Sanchez, *C. R. Acad. Sci.*, 1990, **311**, 1315–1320.
- L. Mathey, M. Paul, C. Copéret, H. Tsurugi and K. Mashima, *Chem. - A Eur. J.*, 2015, **21**, 13454–13461.
- R. Das, R. Sarma and J. B. Baruah, *Inorg. Chem. Commun.*, 2010, **13**, 793–795.
- C. Hennig, A. Ikeda-Ohno, W. Kraus, S. Weiss, P. Pattison, H. Emerich, P. M. Abdala and A. C. Scheinost, *Inorg. Chem.*, 2013, **52**, 11734–11743.
- S. L. Estes, M. R. Antonio and L. Soderholm, *J. Phys. Chem. C*, 2016, **120**, 5810–5818.
- B. Bueken, F. Vermoortele, M. J. Cliffe, M. T. Wharmby, D. Foucher, J. Wieme, L. Vanduyfhuys, C. Martineau, N. Stock, F. Taulelle, V. Van Speybroeck, A. L. Goodwin and D. De Vos, *Chem. - A Eur. J.*, 2016, **22**, 3264–3267.
- S. Øien-Ødegaard, G. C. Shearer, D. S. Wragg and K. P. Lillerud, *Chem. Soc. Rev.*, 2017, **46**, 4867–4876.
- M. Lammert, C. Glißmann and N. Stock, *Dalt. Trans.*, 2017, **46**, 2425–2429.
- J. E. Mondloch, M. J. Katz, N. Planas, D. Semrouni, L. Gagliardi, J. T. Hupp and O. K. Farha, *Chem. Commun.*, 2014, 8944–8946.