A zirconium methacrylate oxocluster as precursor for the low-temperature synthesis of porous zirconium(IV) dicarboxylates†

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The exchange of the monocarboxylate ligand of the zirconium methacrylate oxocluster Zr6O4(OH)4(OMc)12 (OMc = CH2=CH(CH3)COO) with dicarboxylic acids (trans,trans muconic acid and terephthalic acid) leads to porous zirconium dicarboxylates exhibiting the UiO-66 architecture; the mild reaction conditions allow the control of their particle size.

Metal organic frameworks (MOFs) have been intensively studied for more than a decade, owing to their numerous potential applications, mainly in gas adsorption/separation, catalysis or bioapplications.1 Their high surface area and porosity make MOFs very attractive candidates for adsorption of guests, with capacities often exceeding those of carbon materials or zeolites. To date, the search for new MOF architectures has been focused mainly on divalent and trivalent cations of 3d transition metals (Zn, Cu, Fe, Ni, Cr…), 3p metals and lanthanide elements. Higher chemical stability and/or new properties may arise from the use of transition metals with higher oxidation states. Porous hybrid solids based on tetravalent metals are still scarce with mainly a few zirconium diphosphonates with a limited porosity2 and some porous vanadium(IV) dicarboxylates being reported.3 Recently, the first example of a porous zirconium dicarboxylate (UiO-66), composed of eight-hemers of eight-edge or trivalent cations of 3d transition metals (Zn, Cu, Fe, Ni, Cr…) has been shown to be exchangeable proving the robustness of the cluster core and the overall symmetry of the cluster before and after the exchange experiments are the same.4 Also, our group reported the first highly porous titanium(IV) dicarboxylate, which is built up from wheels of eight edge or corner sharing titanium(IV) octahedra.5 However, these latter solids were obtained solvothermally by trial and error, lacking control of the crystallisation and the nature of the final product, which is mainly defined by the knowledge of the inorganic cluster. In order to circumvent this problem, several synthetic routes have been developed recently which use the invariance of the nature and of the structure of the cluster during the exchange of the initial monocarboxylic ligand of the cluster (usually acetates) by polycarboxylates.

This was mainly applied to either copper dimers, trimers of iron/chromium octahedra or tetramers of zinc tetrahedra.1,6 This method presents many advantages, such as the control of the nature and topology of the final product, the possibility to use milder synthetic conditions (for example lower temperature) and thus enabling more control of the particle size, allowing for the preparation of nanoparticles suitable for thin films synthesis or drug delivery.7 Here, we use the known zirconium methacrylate oxocluster Zr6O4(OH)4(OMc)12 to build up porous zirconium dicarboxylates with the UiO-66 topology (Fig. 1).8 This cluster is a member of the organically functionalised tetravalent transition metal oxoclusters family, characterised by an inorganic metal oxide M–O–M core (M = Ti, Zr, Hf…) surrounded by a carboxylate ligand shell,9 which have been extensively used as molecular and structurally well defined building blocks for the synthesis of inorganic–organic hybrid materials.10 The Zr6O4(OH)4 core has been prepared with various monocarboxylate linkers,11 which have been shown to be exchangeable proving the robustness of the oxocluster in solution.12 In these papers, the exchange of the peripheral methacrylate ligands with propionic and isobutyric acid was thoroughly investigated by mono- and bidimensional NMR spectroscopy in solution. These investigations evidenced (i) that the methacrylate groups can be partially or fully (according to the used molar ratios) exchanged by other carboxylates and (ii) that the cluster core is retained upon this exchange. In this regard, heteronuclear multiple bond correlation (HMBC) NMR studies showed that both the cluster core and the overall symmetry of the cluster before and after the exchange experiments are the same.

When considering the synthesis of MOFs, these hexanuclear zirconium oxoclusters can be considered as inorganic

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polytopic secondary building units (SBU) with an unusually high connectivity potential (12 coordination sites) when compared to the Cr or Fe trimers or to the Zn tetramers. These Zr-based building blocks can thus act as connecting points for the formation of new three dimensional networks, including the UiO-66 topology.

This latter solid was synthesised under solvothermal conditions (dimethylformamide (DMF), 120 °C) starting from ZrCl₄ and terephthalic acid precursors. In our case, the metallic salt has been substituted by the Zr₆ methacrylate oxocluster. A systematic study of its reactivity in the presence of two dicarboxylic acids (terephthalic and trans,trans muconic acids) in DMF has been analysed at different temperatures, in the range 25–200 °C and reaction times of between 1 h and 6 days.

With terephthalic acid, UiO-66 is obtained. Its crystallinity is lower when the methacrylate-functionalised cluster is used instead of ZrCl₄ (see Fig. S2†) but diffraction peaks matches those of UiO-66 and its BET surface area is of 905(20) m² g⁻¹ compared to the previously reported surface area of UiO-66 (S_BET = 950(20) m² g⁻¹). With the trans,trans muconic acid, the results are significantly different. Starting from ZrCl₄ as a precursor, and regardless of the temperature (25–200 °C) and synthesis time (1 h–4 days), no crystalline product can be obtained (see Tables S2–S4†), even when mixtures of DMF and water are used. On the contrary, the use of the Zr oxocluster in DMF easily leads to the formation of a white crystalline phase, whatever the stoichiometry (metal/ligand), the concentration, temperature and time (Table S1†). This solid was identified by X-ray powder diffraction data (XRPD) as being isostructural with the cubic UiO-66 structure. Its crystal structure was refined by XRPD with satisfactory figures of merit (Table S5 and Fig. S3†). As expected, this compound is build up from the starting Zr oxocluster surrounded with 12 muconates connecting the cluster to the others, leading to the formation of a network exhibiting octahedral and tetrahedral microporous cages (Fig. 2). (7.5 Å and 12 Å). Surprisingly, the muconate spacer exhibits a disordered cis conformation (Fig. 2), indicating an isomerisation of the starting trans,trans muconic acid during the course of the reaction. Various analyses have been performed and confirm the formula deduced from the structure determination: Zr₆O₂(OH)₄[O₂C–C₄H₄–CO₂]₆·solv (solv = DMF, H₂O) (see ESI†).

X-Ray thermodiffractionometry and TGA indicate that the thermal stability of the Zr muconate is close to 250 °C under air atmosphere (Fig. S4 and S5†), compared to 450 °C for the Zr terephthalate UiO-66, which is in agreement with an easier thermal degradation of the olefin spacer (muconate) with respect to the aromatic spacer (terephthalate). The BET surface area (Fig. S6†) is close to 705 m² g⁻¹, which is lower than the previously reported surface area of UiO-66 (~950 m² g⁻¹), probably due to the lower stability of the Zr muconate solid upon removal of the guest molecules compared with the higher chemical and thermal stability reported for the terephthalate analogue.⁴

In a last step, an ex situ XRPD study of the crystallisation of the muconate solid has been performed at room temperature and 150 °C at different times (1–96 h). The porous crystalline Zr muconate is present at all stages of the synthesis. The mean particle size as a function of the synthesis time has been determined by X-ray powder diffraction using the Debye–Scherrer equation, which estimates the particle size from the half width at mid-height of the Bragg peaks of the solid (see ESI for details†). If, at a synthesis temperature of 150 °C, the particle size is regarded as uniform (~400 nm) whatever the synthesis time (1–96 h), at room temperature, the particle

![Fig. 2](image-url) Crystal structure of the zirconium muconate. Top: view of the two types of cages; bottom: view of the disorder of the muconate.

![Fig. 3](image-url) Top: Ex situ XRPD analysis of the Zr muconate phase (λ = 1.5406 Å) at room temperature; bottom: mean particle size of the Zr muconate phase as a function of time at room temperature, deduced from XRPD analysis using the Scherrer equation.
size varies from 40(5) to 150(10) nm between 1 and 5 h of synthesis (Fig. 3) allowing a careful control of the particle size.

Finally, in order to prove the integrity of the Zr₆ structure with a short range order sensitive technique, analysis by EXAFS was performed on the crystalline Zr₆O₄(OH)₄(OMc)₁₂ cluster and on the MOF sample prepared by the reaction of the Zr₆ methacrylate oxocluster with trans,trans muconic acid in different conditions. The XANES and EXAFS spectra are shown in Fig. S10 and S11.† No significant changes can be observed in the spectra of the MOF in comparison to the muenaconic solid, thus evidencing that the chosen route was efficient in producing Zr₆-based MOFs.

In conclusion, here we have reported the use of a new type of Zr oxocluster building unit with a twelve fold connectivity leading to the controlled synthesis of highly porous Zr dicarboxylates, in addition to the presence of nanoparticles of tuneable size at room temperature. This method paves the way not only for the synthesis of new porous Zr dicarboxylates and their use for applications such as catalysis, gas storage, thin films and drug delivery, but also for the exploration of new structures in MOFs.

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Notes and references


