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Highly augmented, (12,3)-connected Zr-MOF containing hydrated coordination sites for the catalytic transformation of gaseous CO₂ to cyclic carbonates

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Guanghua Jin,^{‡a} Debobroto Sensharma,^{‡a} Nianyong Zhu,^a Sebastien Vaesen^a and Wolfgang Schmitt^a

A porous Zr-based MOF, [Zr₆(BTEB)₄(μ₃-O)₄(μ₃-OH)₄(H₂O)₄], that contains partially hydrated, 12-connected {Zr₆} nodes and extended carboxylate ligands (BTEB³⁻) was synthesized and physicochemically characterised. The resulting (12,3)-connected, 3D framework adopts an uncommon *llj* topology has a large, solvent accessible void volume of *ca.* 79 % of the unit cell volume. The porous structure facilitates the uptake of N₂ and activated samples give rise to BET surface areas of > 1000 m²/g. Furthermore, the porosity and accessibility of Lewis acidic Zr(IV) sites, promote the catalytic transformation of gaseous CO₂ to cyclic carbonates *via* cycloaddition reactions using epoxide reactants whereby solvated MOFs reveal higher catalytic performance than thermally treated samples.

Introduction

Zirconium-based metal-organic frameworks (MOFs) represent a highly desired class of compound, due to their tunable and stable nature, providing porous materials for targeted applications.^{1–6} In Zr-based reaction systems, the formation of oligonuclear oxo-clusters that can serve as secondary building units (SBUs), is favoured by condensation reactions involving Zr(IV) ions. The reaction system generally promotes the formation of highly connected nodes that impart stability to Zr-MOFs.^{7–9} The d⁰ outer electronic configuration of Zr⁴⁺ ions, and the consequent absence of ligand field stabilisation, allows a degree of structural diversity in SBU formation and results in kinetics, amenable to ligand substitution despite the hardness and oxophilicity of the metal ions. Connectivities varying from 6 to 12 for Zr SBUs and a relatively high tolerance to variation in the Zr coordination environment are reported.^{4,5,10–13} Zr nodes have been used to great effect for a variety of applications when combined with extended carboxylate-based ligands to form MOFs.^{14–19} In addition, the use of acetylene spacers to provide linear extension to ligands is a reliable and frequently used strategy to create large, highly accessible framework voids.^{20–24} Porous MOFs based on Zr SBUs are

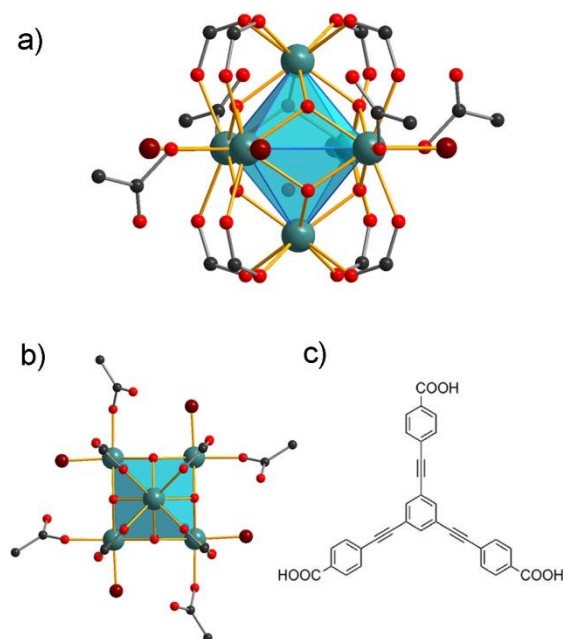


Fig. 1 a) and b) Structure of the {Zr₆(μ₃-O)₄(μ₃-OH)₄(H₂O)₄} oxo-cluster in **TCM-16** showing the carboxylate binding modes that result in the overall 12-connected {Zr₆} SBUs, as well as coordinated water molecules. Colour code: Zr teal, C grey; O red; O-donor atoms of coordinated H₂O molecules are shown in a darker shade of red; c) Tritopic 4, 4', 4''-[1,3,5-benzenetriyl]tris(ethyne-2,1-diyl)]tribenzoic acid (H₃BTEB) ligand used for the preparation of in **TCM-16**.

^a School of Chemistry and SFI AMBER centre, Trinity College Dublin, College Green, Dublin 2, Ireland; [‡] Authors contributed equally
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known for their remarkable gas sorption behaviour (e.g. NU-110, PCN-229, NU-1103), and increasingly for the catalysis of several organic reactions yielding high-value products.^{13,25–35} The use of gaseous chemical feedstocks of naturally abundant compounds, *i.e.* atmospheric CO₂, may allow the development of sustainable approaches for the synthesis of value-added chemical products.³⁶ Chemical means to CO₂ fixation and heterogeneous catalytic approaches involving porous materials to transform CO₂ are particularly intriguing areas of research, whereby CO₂ conversions to carbonates using epoxides are of particular importance due the wide range of product applications in pharmaceutical, medical, polymer and chemical industries.^{37–39} However, many catalytic approaches to carbonates suffer from demanding reaction conditions operating at high temperatures, pressures, or requiring long reaction times.^{40–42} MOFs can represent attractive potential catalysts for the single-step CO₂ transformations to carbonates as the augmented, porous frameworks can provide a high number of active Lewis acidic sites (e.g. Zr⁴⁺ sites) per volume which are accessible to substrates at high diffusion rates.³⁷ We have a strong interest in metal-organic materials that give rise to porosity⁴³ and here, we report the synthesis and characterisation of a new Zr-based MOF that is stabilised by extended tritopic 4,4',4''-[1,3,5-benzenetriyltris(ethyne-2,1-diyl)]tribenzoate ligands (BTEB³⁻). The applied synthetic approach results in a porous, (12,3)-connected net with uncommon **llj** topology containing labile coordination sites. These structural attributes prompted us to investigate its utility as a heterogeneous co-catalyst for the synthesis of cyclic carbonates from CO₂ and epoxides.

Results and Discussion

The MOF, [Zr₆(BTEB)₄(μ₃-O)₄(μ₃-OH)₄(H₂O)₄] (**TCM-16**, TCM: Trinity College Materials), was synthesised using a highly saturated solution of benzoic acid in DMF, and heating ZrCl₄ with H₃BTEB under autogenous pressure at 120 °C for 96 hours. Transparent, rod-shaped single crystals were obtained in yields of *ca.* 55 %.

Single crystal X-ray diffraction studies revealed the adoption of a three-dimensional single-framework structure composed of

hexanuclear Zr⁴⁺ units that are linked by fully deprotonated BTEB³⁻ ligands (Fig. 1). The overall formula for the framework is [Zr₆(BTEB)₄(μ₃-O)₄(μ₃-OH)₄(H₂O)₄]. The inorganic SBU is based on the well-characterised {Zr₆} oxo-cluster, in which six Zr⁴⁺ ions are arranged at the vertices of an octahedron, and μ₃-O²⁻ and μ₃-OH⁻ moieties occupy the centres of the triangular faces of the polygon. However, while the typical SBU as seen in MOFs, such as UiO-66, NU-1000 or the structurally related BTEB³⁻ stabilised MOF-1004, consists uniformly of bidentate carboxylate binding modes, the SBU in **TCM-16** is characterised by monodentate carboxylate binding modes at four positions, whereby the 8-coordination of the Zr⁴⁺ centre is completed by coordinating H₂O ligands.^{1,44,45} This type of coordination environment can allow access to Lewis acidic Zr⁴⁺ sites when the water ligands are displaced during a chemical transformation. Hence, one of the three carboxylate groups on each BTEB³⁻ ligand binds in a monodentate fashion while the other two are bidentate. Each {Zr₆} SBU is connected to 12 separate BTEB³⁻ ligands, and each organic ligand is connected to three {Zr₆} SBUs to form a 3D framework (Fig. 2). The resultant (12,3)-connected net adopts a rather uncommon **llj** topology with the point symbol {4²⁰.6²⁸.8¹⁸}{4³}₄, and structurally relates to a corresponding hafnium-based MOF (Fig. 3).^{46–48}

The structure of **TCM-16** was solved in the tetragonal space group *I4/m*, adopting unit cell dimensions of *a* = 33.102(3) Å, *b* = 33.102(3) Å, and *c* = 21.711(2) Å. The framework as shown in Fig. 2, is highly augmented, with cuboidal channels extending in the direction of the crystallographic *c*-axis and whose square cross-sections are bounded by four BTEB³⁻ ligands and four {Zr₆} SBUs. The channel diameter is 16.8 Å and the coordinated H₂O ligands are highly accessible through these channels. The maximum void diameter is *ca.* 18 Å, and the void volume of the framework structure was determined to be *ca.* 79 % of the unit cell volume. This is in good agreement with the thermogravimetric analysis carried out in a N₂ atmosphere, which shows an initial loss of solvent molecules corresponding to 74.9 wt-% below 140 °C, followed by a ligand decomposition step centred at *ca.* 460 °C. Further supplemental characterisations of **TCM-16** include powder X-ray diffraction and FT-IR spectroscopy studies characterising the phase-purity of as-synthesised bulk samples.

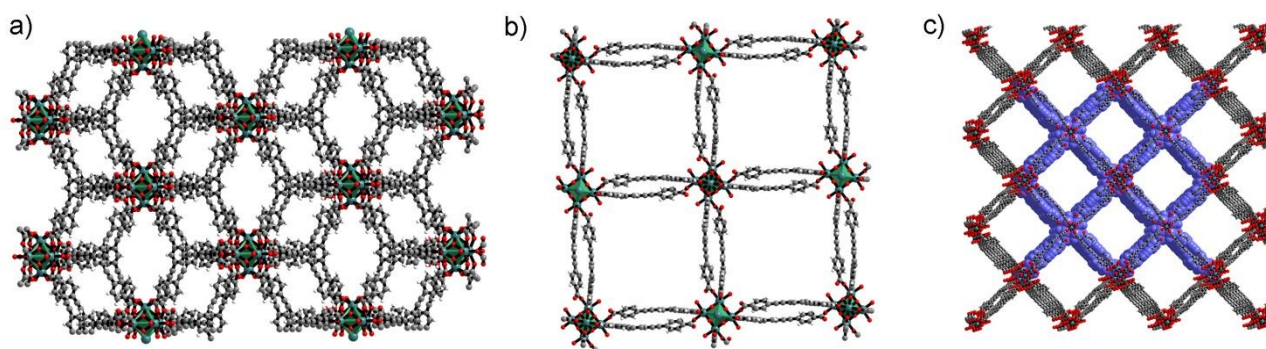


Fig. 2. a) and b) Crystal structure of **TCM-16** viewed in the crystallographic *a*- and *c*-directions, respectively. c) 3x3 supercell of **TCM-16** highlighting the available void space using space-filling representations (purple; 2x2x2 supercell).

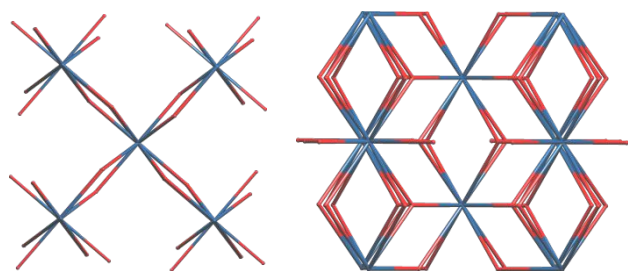


Fig. 3 Topological reduction of the structure of **TCM-16** to the (12,3)-connected **llj** net; View in the crystallographic *c*-direction (*left*) and the *a*-direction (*right*).

The porosity of the MOF was investigated using gas sorption studies (Fig. 4). N_2 sorption analysis at 77 K revealed unambiguously that the porosity can be retained after activation, which is unusual for MOFs solely containing highly extended BTEB³⁻ ligands.^{23,24,49,50} The resulting isotherm shows clear microporosity and a steep gas uptake at low partial pressures. A surface area of 1091 m²/g was obtained through BET analysis. CO_2 sorption isotherms measured at 278 K, 293 K, and 308 K, reveal CO_2 uptakes at 1 bar of 84 cc/g, 46 cc/g, and 17 cc/g, respectively (ESI). It is noteworthy that the activation procedure of **TCM-16** is not trivial (ESI) and requires care as the removal of the coordination H_2O molecules in **TCM-16** can conceptually give rise to 'open metal sites' upon thermal treatment. However these sites, are expected to get instantaneously occupied by the monodentate carboxylate groups of the BTEB³⁻ ligands that locate in close vicinity. This structural transition will undoubtedly be associated with amorphisation and loss of porosity.

Thus, the structure of **TCM-16** containing labile Lewis-acidic Zr^{4+} sites, lends itself to solution studies, whereby the terminal H_2O molecules are replaced by substrates to promote catalytic activity under turnover conditions. Geometrical restrains

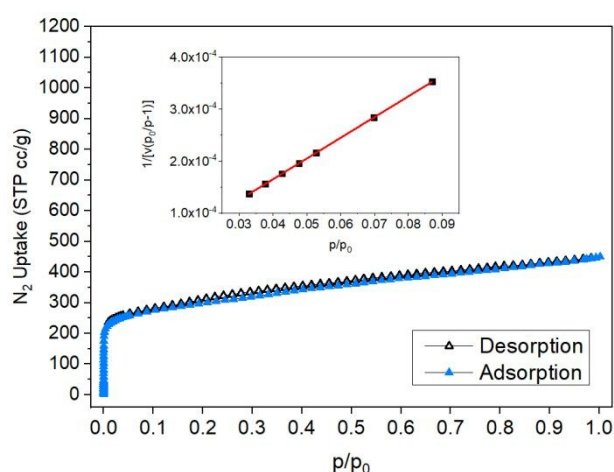
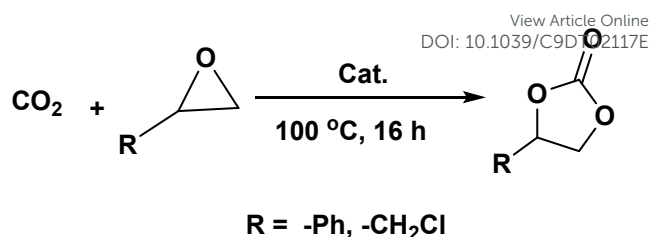


Fig. 4. N_2 (77 K) low-pressure adsorption and desorption isotherms obtained for **TCM-16**, inset: Multi-point BET fit; slope = 3.186, intercept = 4.307×10^{-3} , correlation coefficient, $r = 0.999996$, C (constant) = 740.649.



Scheme 1. Catalytic cycloaddition of CO_2 to cyclic carbonates using styrene oxide and (chloromethyl)oxirane.

within the channels may further increase the local substrate concentrations in proximity to the catalytically active Zr^{4+} sites in the MOF. With these considerations in mind, preliminary experiments were conducted using **TCM-16** as a porous, heterogeneous matrix for the cycloaddition between CO_2 and oxirane derivatives to produce cyclic organic carbonates (Scheme 1). The catalytic test reactions were carried out for 16 hours using styrene oxide or (chloromethyl)oxirane and CO_2 (1 atm, balloon pressure) in the presence of 0.5 mol% of **TCM-16** and 1 mol% of tetrabutylammonium bromide (TBAB) at 100 °C. The yields of the produced cyclic carbonates were determined by 1H NMR spectroscopy.

In the presence of **TCM-16**, the yields of the cyclic carbonate products increased significantly whereby freshly prepared hydrated MOF samples led to almost quantitative transformations reaching styrene carbonate and chloropropene carbonate yields of 92.8 and 99.5 %, respectively (Table 1). When **TCM-16** was thermally treated at 100 °C under reduced pressure for 4 hours, significantly lower yields of 19.4 and 58.1 % were obtained. In contrast, as-prepared **TCM-16** samples, even performed in the absence of TBAB, resulted in styrene carbonate and chloropropene carbonate yields of 61.3 and 78.1 %, respectively. Solvated samples of **TCM-16** maintain their structural integrity as demonstrated by X-ray powder diffraction (ESI, Fig. S.6), are recyclable and retain their high activity in consecutive catalysis experiments (Table 1, entry 5). Significant leaching of Zr ions from **TCM-16** was not detectable (Energy-dispersive X-ray spectroscopy using dried post-catalytic reaction solutions). The experimental observations of these catalysis experiments are in-line with studies that demonstrate that $\{Zr-H_2O\}$ moieties in MOFs can effectively promote the investigated cycloaddition reaction whereas dehydrated, closed MOF structures or collapsed MOF structures are expected to reveal lower activities.⁵¹ Further, as the gas sorption studies demonstrate, thermally treated samples of **TCM-16** have a tendency to lose their microporosity, thus reducing the availability of active sites per volume and resulting in lower catalytic activity. The outlined catalytic transformations are expected to follow the general mechanism for the cycloaddition of CO_2 using epoxides³⁷ whereby the metal sites facilitate interactions with

Table 1. TCM-16-catalyzed cycloaddition of CO₂ using epoxides, reaction conditions: epoxide (5 mmol), TCM-16 (0.5 mol%), CO₂ (1 atm, balloon pressure), 100 °C.^a TCM-16 was treated at 100 °C for 4 hours under vacuum prior to the use as catalyst; ^b Moles of cyclic carbonate produced per mole of catalyst; ^c Catalyst recyclability of TCM-16 was tested under the same reaction conditions; TCM-16 retained the same activities after three runs and yields of the cyclic carbonate of 99.5 % were obtained; Substrates: styrene oxide (R = -Ph) or (chloromethyl)oxirane (R = -CH₂Cl).

Entry	Substrate, R=	TBAB Co-catalyst	Yield	TON ^b
1	-Ph	--	61.3 %	123
2	-Ph	1 mol%	92.8 %	186
3 ^a	-Ph	1 mol%	19.4 %	39
4	-CH ₂ Cl	--	78.1 %	156
5 ^c	-CH ₂ Cl	1 mol%	99.5 %	199

the O-atom of the oxirane moiety prior to the ring-opening and followed by CO₂ insertion to form the carbonate product.

Conclusions

In summary, we report the synthesis and characterization of a porous MOF, TCM-16 that is composed of hexanuclear {Zr₆(μ₃-O)₄(μ₃-OH)₄(H₂O)₄} SBUs which provide 12-connected nodes. Assembly in the presence of the trifunctional benzoate ligand, BTEB³⁻, promotes the formation of a (12,3)-connected net with an uncommon *llj* topology. The MOF structure maintains its porous nature upon removal of constitutional solvent molecules and facilitates the uptake of N₂ giving an experimental BET surface area of 1091 m²/g. Notably are four coordination H₂O molecules at the {Zr₆} SBUs which may provide kinetically labile binding sites accessible for catalytic transformations. We demonstrate that TCM-16 promotes the cycloaddition between gaseous CO₂ and oxirane derivatives to produce cyclic organic carbonates.

Experimental

Methods and Materials

Commercially available chemicals were used as obtained in high purity and from standard chemical suppliers without further purification. The 4,4',4''-[1,3,5-benzenetriyltris(ethyne-2,1-diyl)]tribenzoic acid (H₃BTEB) ligand was prepared using a modified literature procedure.⁵² Single-crystal X-ray diffraction studies were performed using a Bruker APEX2 Duo diffractometer equipped with a microfocus Cu-Kα source (λ = 1.5418 Å) and a Bruker SMART APEX2 area detector. Intensity data was corrected for absorption by multi-scan methods using SADABS.⁵³ The structures were solved and refined using SHELXT⁵⁴ and SHELXL⁵⁵ as implemented in Olex2.⁵⁶ H- positions were calculated using a riding model. The structure contains large solvent accessible void volume in which solvent molecules could not be located reliably. To account for this, the Platon-SQUEEZE routine was used to calculate the void volume and re-generate the reflection file by excluding the diffraction

contributions of these unlocated solvent molecules.⁵⁷ A solvent mask accounting for 2421 electrons was found in a volume of 19095 Å³, in one void per unit cell. This is consistent with the presence of ca. 30 DMF molecules per formula unit or a H₂O/DMF solvent mixture. Crystallographic data can be obtained from The Cambridge Crystallographic Data Centre (CCDC number 1916002) via www.ccdc.cam.ac.uk/data_request/cif.

Infrared data in the 4000-650 cm⁻¹ region were obtained using a PerkinElmer Spectrum One FT-IR spectrometer with a universal Attenuated Total Reflectance (ATR) sampling accessory. Thermogravimetric analyses were performed using a Perkin Elmer Pyris 1 TGA instrument that had been previously calibrated using nickel and iron standards. Samples were heated in a ceramic crucible under a nitrogen atmosphere from room temperature to ca. 700 °C, at a rate of 5 °C/min.

Synthesis of [Zr₆(BTEB)₄(μ₃-O)₄(μ₃-OH)₄(H₂O)₄] (TCM-16)

[Zr₆(BTEB)₄(μ₃-O)₄(μ₃-OH)₄(H₂O)₄] was synthesised by dissolving 28.8 mg of ZrCl₄ (0.12 mmol), 46.4 mg of H₃BTEB (0.09 mmol), and 1.465 g (12 mmol) of benzoic acid in 8 mL of dimethylformamide (DMF) in a closed vial and heating the reaction mixture to 120 °C for four days. Colourless crystals of [Zr₆(BTEB)₄(μ₃-O)₄(μ₃-OH)₄(H₂O)₄] solv were obtained, washed with acetone and stored at ambient conditions. Yield: 31 mg, ca. 55 % based on Zr. Microanalytical data for C₁₃₂H₇₂O₃₆Zr₆ (including additional 9.5 H₂O and 0.5 DMF solvent molecules), calc (%): C 53.64, H 3.19, N: 0.23; found: C 53.46, H 2.64, N 0.15. For further characterisation see ESI.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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