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**Zr(IV) and Hf(IV) based metal–organic frameworks with reo-topology†‡**Volodymyr Bon,<sup>a</sup> Volodymyr Senkovskyy,<sup>b</sup> Irena Senkovska<sup>\*a</sup> and Stefan Kaskel<sup>a</sup>

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**Zr and Hf based MOFs with enhanced pore accessibility for large molecules and good hydrothermal stability were obtained using a bent dithienothiophene dicarboxylate and Zr<sup>4+</sup> or Hf<sup>4+</sup> source. A modulator (benzoic acid) facilitates formation of an eight-connecting cluster leading to a new framework which adopts reo topology.**

During the last two decades, a rapid development of metal–organic frameworks (MOFs) chemistry was achieved exploring the widely applicable modular construction principles and the broad application potential.<sup>1–4</sup> However, one significant limitation for the use of many highly porous MOF materials under ambient conditions is the low hydrolytic stability. A promising step forward was the discovery of the 12 coordinated zirconium cluster Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(CO<sub>2</sub>)<sub>12</sub>, recently reported by Cavka *et al.*<sup>5</sup> The MOF structure formed with a linear 1,4-benzenedicarboxylate ligand (UiO-66) shows ultimate thermal and especially chemical stability, and could be successfully applied in catalysis,<sup>6</sup> hydrogen generation,<sup>7</sup> and selective adsorption.<sup>8</sup> Taking into consideration the low toxicity of Zr containing compounds,<sup>9</sup> Zr based MOFs may be also very suitable as drug delivery agents.

Since the discovery of UiO-66, numerous isorecticular MOFs, namely UiO-67, UiO-68, PIZOF-1–PIZOF-8, have been reported.<sup>10</sup> All the above-mentioned materials form a 12-connected network with **fcu** topology limiting the availability of pore shape and size, and especially pore windows size. Access to the internal structure of UiO-type materials is limited by triangular windows with diameters of 6, 8 and 10 Å for UiO-66, UiO-67 and UiO-68 respectively.<sup>5</sup> Additionally, utilization of longer linear linkers gives rise to interpenetration.<sup>10</sup> The latter is a limitation for a wide spectrum of larger molecules which could be stored and released from such MOFs.

The aim of this work was to make use of the relatively stable Zr–carboxylate bond and at the same time to enhance the accessibility of the pores for large molecules (for example for drug molecules). We pursued a strategy that focuses on reducing the ability of the [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>]<sup>12+</sup> cluster<sup>11</sup> to coordinate multifunctional linker molecules, and as a beneficial side effect, open metal sites in the Zr containing structure could be created.

Synthetically, this strategy was successful using a bent thiophene dicarboxylate linker, namely dithieno[3,2-*b*;2',3'-*d*]thiophene-2,6-dicarboxylate (DTTDC). Carboxylic groups of this molecule are spaced at a distance of 9.16 Å and with an angle of 148.6°. The new material, named DUT-51(Zr), containing an eight-connecting Zr-cluster was obtained in a solvothermal reaction of ZrCl<sub>4</sub>, DTTDC in DMF and has the overall composition [Zr<sub>6</sub>O<sub>6</sub>(OH)<sub>2</sub>(DTTDC)<sub>4</sub>(BC)<sub>2</sub>(DMF)<sub>6</sub>](DMF)<sub>12</sub>(H<sub>2</sub>O)<sub>19</sub> (BC = benzoic acid and DMF = *N,N*-dimethylformamide).

Moreover, using the same synthesis conditions, but HfCl<sub>4</sub> as a metal source, the isomorphous Hf containing analogue with composition [Hf<sub>6</sub>O<sub>6</sub>(OH)<sub>2</sub>(DTTDC)<sub>4</sub>(BC)<sub>2</sub>(DMF)<sub>6</sub>](DMF)<sub>12</sub>(H<sub>2</sub>O), DUT-51(Hf), could be produced. The chemical composition of both compounds was derived from TG, elemental, single crystal and NMR analysis (Section S3, ESI†).

The presence of benzoic acid during the synthesis is essential for the MOFs formation. Without BC, only an amorphous product could be obtained (Fig. S3, ESI†).

Crystal structures of DUT-51 were determined by single crystal X-ray diffraction using synchrotron radiation.<sup>10</sup> The SBU contains 6 octahedrally arranged Zr/Hf atoms interconnected by 8 μ<sub>3</sub>-oxygen atoms (Fig. 1a).

Each SBU is interconnected by 8 DTTDC molecules forming an 8-connected robust 3D network with **reo** topology (Fig. 1d, Fig. S1 and S2 (ESI†)).<sup>12</sup> As derived from elemental analysis, TG, and NMR investigations, another 8 coordination places of the cluster, located in the equatorial plane of Zr<sub>6</sub>/Hf<sub>6</sub> octahedron, are occupied by 6 solvent molecules (DMF) and 2 benzoic acid (BC) molecules used as modulator (Fig. 1b) (for more information see Section S3, ESI†).<sup>13</sup> However, only oxygen atoms of DMF and BC could be located crystallographically. As a result of such combination of SBU and the bent linker, octahedral (15.6 Å in diameter) and cubo-octahedral (with 18.8 Å in diameter) pores are formed (Fig. 1c). The octahedral pores are connected *via* triangular windows with 8 cubo-octahedral pores. The latter is surrounded by 12 SBUs, interconnected by 24 DTTDC linkers in such a way that sulfur atoms of the middle thiophene rings are directed towards the interior of the pore (Fig. 1c).

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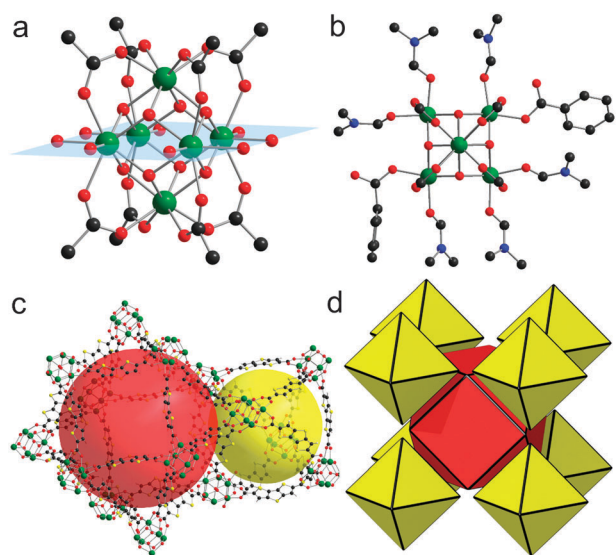
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‡ Electronic supplementary information (ESI) available: General procedures, materials and instrumentation; single-crystal X-ray diffraction analysis; powder X-ray diffraction, thermogravimetric analysis, physisorption isotherms; dye adsorption experiments. CCDC 872966 and 872967. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc34246d



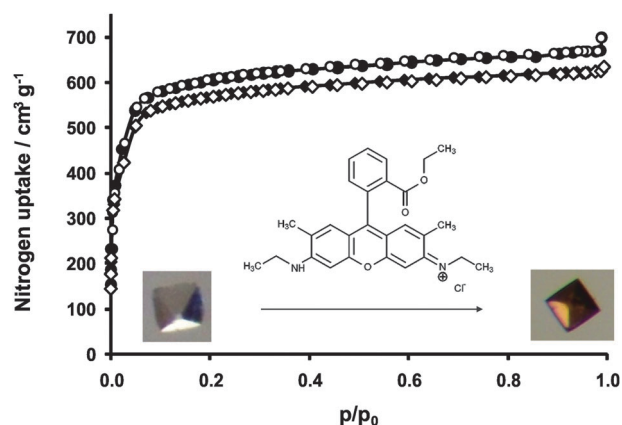
**Fig. 1** Crystal structure of DUT-51: (a)  $[\text{Zr}_6\text{O}_6(\text{OH})_2]^{10+}$  cluster coordinating 8 DTTDC linkers (only oxygen atoms of solvent molecules and benzoic acid are presented); (b) cluster surrounding (the coordinated DMF and benzoic acid molecules are simulated in Material Studio 5.0); (c) octahedral pore (yellow sphere) and cubo-octahedral pore (red sphere). The spheres represent the free pore volume; (d) pore packing. (The atoms are represented: carbon in grey, oxygen in red, sulfur in yellow, zirconium in green. Hydrogen atoms are omitted.)

The cubo-octahedral pore has 6 square and 8 triangular windows. The diameters of the circles, which can be inscribed in the mentioned windows, are 9 and 4.2 Å, respectively. In the crystal structure, each cubo-octahedral pore is surrounded by 6 identical pores, sharing square faces of cubo-octahedron (Fig. 1d).

After removal of guest solvent molecules, the potential solvent accessible void, calculated by PLATON,<sup>14</sup> is 78.1% for DUT-51(Zr) and 78.0% for DUT-51(Hf). Theoretical BET specific surface area, calculated using SURFACE program,<sup>15</sup> from the crystal structure after exclusion of solvent molecules amounts to 2671  $\text{m}^2 \text{g}^{-1}$  for DUT-51(Zr) and 2106  $\text{m}^2 \text{g}^{-1}$  for DUT-51(Hf).

To prove the porosity of the compounds, nitrogen, hydrogen and methane physisorption isotherms were measured. The nitrogen adsorption isotherms measured at 77 K on samples activated thermally at 120 °C under vacuum reach the saturation value of 671  $\text{cm}^3 \text{g}^{-1}$  for DUT-51(Zr) and 625  $\text{cm}^3 \text{g}^{-1}$  for DUT-51(Hf) (Fig. 2). It should be noted that the coordinated benzoic acid molecules cannot be removed from the cluster without collapse of the structure, which reduces the amount of open metal sites. The specific surface area, calculated from nitrogen adsorption isotherms using a multipoint BET model,<sup>16</sup> amounts to 2335  $\text{m}^2 \text{g}^{-1}$  for DUT-51(Zr) and 1859  $\text{m}^2 \text{g}^{-1}$  for DUT-51(Hf). The total pore volume is 1.08  $\text{cm}^3 \text{g}^{-1}$  ( $p/p_0 = 0.99$ ) for DUT-51(Zr) and 0.97  $\text{cm}^3 \text{g}^{-1}$  ( $p/p_0 = 0.99$ ) for DUT-51(Hf).

Hydrogen excess adsorption at 77 K for DUT-51(Zr) (Fig. S10, ESI†) shows a maximum uptake at 40 bar of 37.3  $\text{mg g}^{-1}$  (3.6 wt%). The total amount adsorbed at 100 bar is 68.3  $\text{mg g}^{-1}$ . The maximum excess of methane adsorbed on DUT-51(Zr) is 0.12  $\text{g g}^{-1}$  at 80 bar and 298 K, equivalent to 112  $\text{cm}^3 \text{cm}^{-3}$



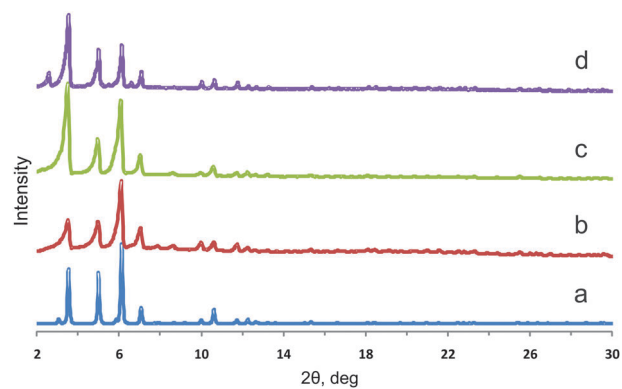
**Fig. 2** Nitrogen adsorption (closed symbols) and desorption (open symbols) isotherms (77 K) on DUT-51(Zr) (circles) and DUT-51(Hf) (diamonds). Inset: color change of DUT-51(Zr) during the rhodamine 6G adsorption.

taking the crystallographic density into account. The total amount adsorbed at 140 bar is 0.24  $\text{g g}^{-1}$  (Fig. S9, ESI†).

DUT-51(Zr) and DUT-51(Hf) are stable against hydrolysis and can be stored under ambient conditions without loss of crystallinity or porosity. The hydrothermal stability of both compounds was demonstrated by soaking dried samples in water for 12 hours. The powder XRD patterns, measured after this time, show no significant loss of crystallinity (see Fig. 3 and Section S6, ESI†). Nitrogen adsorption isotherms measured after water treatment reach saturation at 520  $\text{cm}^3 \text{g}^{-1}$  by DUT-51(Zr) and 471  $\text{cm}^3 \text{g}^{-1}$  by DUT-51(Hf) (Fig. S11, ESI†).

The thermal analyses (Section S7, ESI†) show that both materials are stable up to 150 °C. Higher temperatures cause network collapse due to removal of two coordinated benzoic acid from the cluster.

The water adsorption isotherm measured at 25 °C (Fig. S12, ESI†) points on rather hydrophobic nature of pore interior, the main adsorption occurs at  $p/p_0$  higher than 0.5. Thus, the benzoic acid molecules coordinated to the cluster have a shielding function and protect the cluster from the water attack. For UiO-66 the water vapor adsorption starts at a significantly lower  $p/p_0$  value of 0.2.<sup>17</sup> The maximum uptake of 690  $\text{cm}^3 \text{g}^{-1}$  is comparable to that of HKUST-1.<sup>18</sup>



**Fig. 3** PXRD patterns of DUT-51(Zr): calculated from the single crystal X-ray structure (a), as made phase (b), activated at 120 °C (c), after 12 hours soaking in water (d).

The pore accessibility for large molecules was evaluated using dye adsorption experiments in the liquid phase (see Section S9, ESI†). The adsorption could be observed for all molecules used in this study (adsorption of rhodamine 6G is shown in Fig. 2), demonstrating the potential for processing of larger drug molecules. Also the C<sub>60</sub> fullerene can be adsorbed on DUT-51.

In summary, using the bent DTTDC linker in combination with a modulator (benzoic acid) in the synthesis, we were able to decrease the connectivity of the Zr cluster in MOF. As a result novel, moisture stable material Zr<sub>6</sub>O<sub>6</sub>(OH)<sub>2</sub>(DTTDC)<sub>4</sub>(BC)<sub>2</sub> (DUT-51(Zr)) and isotopic Hf<sub>6</sub>O<sub>6</sub>(OH)<sub>2</sub>(DTTDC)<sub>4</sub>(BC)<sub>2</sub> (DUT-51(Hf)) with extra-wide and accessible pores were obtained. The benzoic acid acts not only as a crystallization agent, but is also essential for the structure formation.

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## Notes and references

§ Crystal data after SQUEEZE (synchrotron radiation,  $\lambda = 0.88561 \text{ \AA}$ ): DUT-51(Zr), [Zr<sub>6</sub>O<sub>6</sub>(OH)<sub>2</sub>(DTTDC)<sub>4</sub>(BC)<sub>2</sub>(DMF)<sub>6</sub>](DMF)<sub>12</sub>(H<sub>2</sub>O)<sub>19</sub>,  $M_r = 3706.77$ , cubic  $Fm\bar{3}m$ ,  $a = 49.964(6) \text{ \AA}$ ,  $V = 124726(25) \text{ \AA}^3$ ,  $Z = 24$ ,  $D_c = 1.184 \text{ g cm}^{-3}$ , 6283 independent reflections observed,  $R_1 = 0.0467$  ( $I > 2\sigma(I)$ ),  $wR_2 = 0.1334$  (all data), and GOF = 1.096; DUT-51(Hf), [Hf<sub>6</sub>O<sub>6</sub>(OH)<sub>2</sub>(DTTDC)<sub>4</sub>(BC)<sub>2</sub>(DMF)<sub>6</sub>](DMF)<sub>12</sub>(H<sub>2</sub>O),  $M_r = 3906.10$ , cubic  $Fm\bar{3}m$ ,  $a = 49.840(6) \text{ \AA}$ ,  $V = 123804(26) \text{ \AA}^3$ ,  $Z = 24$ ,  $D_c = 1.257 \text{ g cm}^{-3}$ , 6239 independent reflections observed,  $R_1 = 0.0355$  ( $I > 2\sigma(I)$ ),  $wR_2 = 0.1046$  (all data), and GOF = 1.100. CCDC 872966 and 872967.

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