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# Zr- and Hf-Based Metal–Organic Frameworks: Tracking Down the Polymorphism

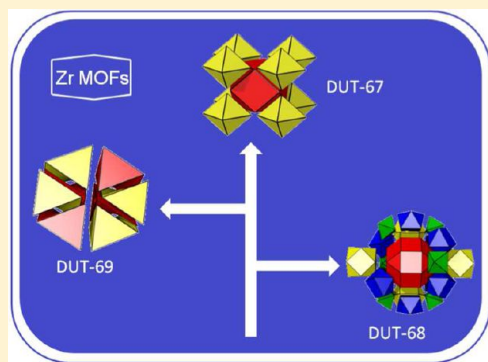
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## Supporting Information

**ABSTRACT:** Six novel Zr(IV)- and Hf(IV)-based MOFs, namely DUT-67, DUT-68, and DUT-69 (DUT, Dresden University of Technology) were obtained using a modulated synthesis approach with the acetic acid as a modulator and the bent 2,5-thiophenedicarboxylate ( $\text{tdc}^{2-}$ ) as a ligand. The modulator not only increases the size of the MOF crystallites but also plays a role of a structure directing agent, affecting both the secondary building unit (SBU) connectivity and topology of the resulting frameworks. The structure of DUT-67 is based on the **reo** underlying net, characteristic for its cuboctahedral and octahedral pores and is therefore isorecticular to DUT-51. The DUT-68 material has a more complicated hierarchical pore system including rhombicuboctahedral mesopore, surrounded by cuboctahedral, square-antiprismatic and octahedral microcages. DUT-69 is the first example of Zr-based MOF containing 10-connected SBU. DUT-69 has **bct** topology, possessing octahedral cages and channels running along one crystallographic direction. In accordance with X-ray single crystal analysis, the pores of DUT-67 and DUT-68, which were obtained at high modulator concentrations, are partially occupied by additional clusters. All novel materials are found to be robust, hydrophilic, chemically, and thermally stable. The BET specific surface area amounts to 1064 and 810  $\text{m}^2\cdot\text{g}^{-1}$  for DUT-67(Zr) and DUT-67(Hf), 891 and 749  $\text{m}^2\cdot\text{g}^{-1}$  for DUT-68(Zr) and DUT-68(Hf), and 560 and 450  $\text{m}^2\cdot\text{g}^{-1}$  for DUT-69(Zr) and DUT-69(Hf), respectively.



## INTRODUCTION

Functional porous materials, such as metal–organic frameworks (MOFs), are envisioned for numerous applications, for example, in gas storage<sup>1</sup> and separation,<sup>2,3</sup> catalysis,<sup>4</sup> sensor technologies,<sup>5</sup> and optical devices.<sup>6</sup> In the versatile MOF chemistry Zr-based materials are of special interest because of their robustness, thermal and chemical stability, low toxicity as well as tolerance to the incorporation of functional groups.<sup>7,8</sup> Despite the growing popularity of Zr-based MOFs since UiO-66 discovery in 2008, the reports on topologically new structures involving Zr are quite rare<sup>9,10</sup> and only two porous Hf-containing MOFs have been described so far.<sup>11,12</sup>

The UiO-66 and related isorecticular structures are built up from 12-connected clusters linked by linear linker molecules, resulting in the formation of 3D uninodal frameworks with **fcu** underlying topology. Recently, a new Zr-based secondary building unit (SBU) has been discovered, which can be derived from  $\text{Zr}_6\text{O}_4(\text{OH})_4^{12+}$  by decreasing the connectivity from 12 to 8. For instance, utilizing a 4-connected porphyrine based linker, the 4,8-connected frameworks (MOF-545<sup>9</sup> or PCN-222<sup>10</sup>) with the **csq-a** topology were obtained. By using a bent dithienothiophene-based ligand, the uninodal 8-connected framework (DUT-51) with the **reo** topology was recently discovered in our group.

The main limitation in the development of Zr MOFs chemistry is, among others, the determination of the crystal

structure, since the products are mostly microcrystalline powders. It was recently shown that the size of Zr MOF crystallites can be controlled by using additional organic or inorganic acid as modulator.<sup>13</sup> Recently, we have shown for DUT-51 that if the monocarboxylic acid is used as modulator, it can be involved in the MOF structure and acts not only as a crystal growth inhibitor, but also as a structure directing agent.

In this work, the role of the modulator has been extended further. Namely, the modulator concentration affects the topology of the frameworks giving rise to MOF polymorphs with different pore systems. Furthermore, crystal structure analysis suggests the incorporation of the additional SBUs into the pores of the framework: the Zr/Hf based MOFs obtained using high modulator concentrations are able to encapsulate additional cluster units *in situ* during the MOF synthesis.

Herein, we report on a series of novel Zr and Hf based topologically different materials DUT-67, DUT-68, and DUT-69 involving bent 2,5-thiophenedicarboxylate ( $\text{tdc}^{2-}$ ) ligand, which were obtained by applying a modulated synthesis approach. It was shown, that the compounds are porous, hydrolytically stable and acid resistant, which qualifies them as materials with high application potential.

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## ■ EXPERIMENTAL SECTION

ZrCl<sub>4</sub> (98% purity) and HfCl<sub>4</sub> (98% purity) were purchased from Sigma Aldrich and used as received. 2,5-thiophenedicarboxylic acid (H<sub>2</sub>tdc) was obtained from TCI, dimethylformamide (DMF) (p.a. purity) from Sigma Aldrich, and *N*-methyl-2-pyrrolidone (99%) from ACBR GmbH. Acetic acid (100%) was purchased from VWR. The elemental analysis for C, H, and N were performed with CHNS 932 analyzer (LECO). Nitrogen physisorption experiments were performed at 77K up to 1 bar on Quadrasorb apparatus (Quantachrome Co.). Water vapor physisorption was investigated at 298 K using Hydrosorb 1000 apparatus (Quantachrome Co.) with equilibration time of 300 s. The thermogravimetric analysis was carried out on air using a Netzsch STA 409 PC Luxx thermal analyzer and heating rate of 5°/min in the temperature region from 20 up to 1000 °C. Powder X-ray diffraction data were collected on a STOE STADI P diffractometer with Cu-Kα1 radiation ( $\lambda = 1.5405 \text{ \AA}$ ) at room temperature.

**Synthesis of DUT-67.** ZrCl<sub>4</sub>/HfCl<sub>4</sub> (230 mg/320 mg, 1 mmol) was dissolved in the mixture of DMF (12.5 mL) and NMP (12.5 mL) by sonication for 10 min. 2,5-Thiophenedicarboxylic acid (H<sub>2</sub>tdc) (110 mg, 0.67 mmol) was added to resulting solution and sonicated additional 5 min. After that acetic acid (7 mL, 117 mmol) was added to the solution and sonicated for 10 min. The resulting mixture was distributed to 10 Pyrex tubes, which were subsequently tempered at 120 °C for 48 h. The resulted powder was separated by centrifugation and washed several times with DMF until supernatant solution became colorless. The powder was filtered and dried under argon atmosphere for half an hour. Yield: 224 mg (71.5%) for DUT-67(Zr) and 259 mg (63.9%) for DUT-67(Hf).

The single crystals of DUT-67 were obtained using the same procedure, but 10 mL of acetic acid instead of 7 mL were added.

Analytical data for “as-made” DUT-67(Zr) phase Zr<sub>6</sub>O<sub>6</sub>(OH)<sub>2</sub>(tdc)<sub>4</sub>(Ac)<sub>2</sub>·6.5H<sub>2</sub>O·4.7DMF: Calcd C 26.10%, H 3.23%, N 3.40%, S 6.62%; Found C 25.73%, H 2.85%, N 3.77%, S 6.66%. Analytical data for thermally (120 °C) dry phase Zr<sub>6</sub>O<sub>6</sub>(OH)<sub>2</sub>(tdc)<sub>4</sub>(ac)<sub>2</sub>·3.1H<sub>2</sub>O·0.6DMF: Calcd C 22.72%, H 1.69%, N 0.53%, S 8.14%; Found C 22.97%, H 1.98%, N 0.79%, S 8.43%.

Analytical data for as-made DUT-67(Hf) phase Hf<sub>6</sub>O<sub>6</sub>(OH)<sub>2</sub>(tdc)<sub>4</sub>(Ac)<sub>2</sub>·3.4H<sub>2</sub>O·6.1DMF: Calcd C 22.18%, H 2.63%, N 3.41%, S 5.12%; Found C 22.00%, H 2.43%, N 3.55%, S 4.91%. Analytical data for thermally (120 °C) dry phase Hf<sub>6</sub>O<sub>6</sub>(OH)<sub>2</sub>(tdc)<sub>4</sub>(ac)<sub>2</sub>·0.5DMF: Calcd C 17.39%, H 0.97%, N 0.34%, S 6.30%; Found C 17.78%, H 1.36%, N 0.30%, S 6.25%.

**Synthesis of DUT-68.** ZrCl<sub>4</sub>/HfCl<sub>4</sub> (230 mg/320 mg, 1 mmol) was dissolved in DMF (25 mL) by sonication for 10 min. H<sub>2</sub>tdc (258 mg, 1.5 mmol) was added to resulting solution, and the mixture was sonicated additional 5 min. After that acetic acid (11 mL, 183 mmol) was added and the mixture was sonicated for further 10 min. The reaction mixture was distributed to 12 Pyrex tubes, which were subsequently tempered at 120 °C for 72 h. The washing and drying procedure was the same as applied to DUT-67. Yield: 384 mg (53.9%) for DUT-67(Zr) and 453 mg (52.3%) for DUT-67(Hf). The single crystals of DUT-68(Zr) were obtained using the same synthetic protocol, but utilizing larger amount of modulator.

Analytical data for as-made DUT-68(Zr) phase Zr<sub>6</sub>O<sub>6</sub>(OH)<sub>2</sub>(tdc)<sub>4.5</sub>(Ac)<sub>2</sub>·7H<sub>2</sub>O·7.75DMF: Calcd C 28.60%, H 3.78%, N 4.95%, S 6.58%; Found C 28.53%, H 3.85%, N 4.88%, S 6.65%. Analytical data for thermally (120 °C) dry phase Zr<sub>6</sub>O<sub>6</sub>(OH)<sub>2</sub>(tdc)<sub>4.5</sub>(Ac)<sub>2</sub>·0.5DMF: Calcd C 23.84%, H 1.16%, N 0.48%, S 9.37%; Found C 23.97%, H 1.24%, N 0.35%, S 9.24%.

Analytical data for as-made DUT-68(Hf) phase Hf<sub>6</sub>O<sub>6</sub>(OH)<sub>2</sub>(tdc)<sub>4.5</sub>(Ac)<sub>2</sub>·4.5H<sub>2</sub>O·7.3DMF: Calcd C 23.14%, H 2.83%, N 3.87%, S 5.47%; Found C 22.94%, H 2.62%, N 3.76%, S 5.26%. Analytical data for thermally (120 °C) dry phase Hf<sub>6</sub>O<sub>6</sub>(OH)<sub>2</sub>(tdc)<sub>4.5</sub>(Ac)<sub>2</sub>·4.2H<sub>2</sub>O·0.3DMF: Calcd C 16.91%, H 1.17%, N 0.2%, S 6.79%; Found C 17.28%, H 1.54%, N 0.18%, S 7.03%.

**Synthesis of DUT-69.** ZrCl<sub>4</sub> or HfCl<sub>4</sub> (230/320 mg, 1 mmol) was dissolved in DMF (50 mL) by sonication for 10 min. H<sub>2</sub>tdc (172 mg, 1

mmol) was added to the solution and sonicated additional 5 min. After that acetic acid (3 mL, 50 mmol) was added to the mixture and sonicated for 10 min. The mixture was distributed to 10 Pyrex tubes, which were subsequently tempered at 120 °C for 12 h. The precipitated crystalline powder was centrifuged and washed several times with DMF. The powder was filtered and dried under argon atmosphere for 30 min. Yield: 228 mg (52.4%) for DUT-69(Zr) and 348 mg (58.2%). Single crystals of DUT-69(Zr) and DUT-69(Hf) were obtained using the same procedure that was used for DUT-69(Zr) but utilizing 25 mL of solvent and 6 mL of modulator (acetic acid).

Analytical data for as-made DUT-69(Zr) phase Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(tdc)<sub>5</sub>(Ac)<sub>2</sub>·11.7H<sub>2</sub>O·4.1DMF: Calcd C 25.76%, H 3.37%, N 2.66%, S 7.43%; Found C 24.91%, H 2.44%, N 3.53%, S 6.50%. Analytical data for thermally (120 °C) dry phase Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(tdc)<sub>5</sub>(Ac)<sub>2</sub>·4.55H<sub>2</sub>O·1.55DMF: Calcd C 25.18%, H 2.18%, N 1.18%, S 8.70%; Found C 24.82%, H 1.81%, N 1.01%, S 8.32%.

Analytical data for as-made DUT-69(Hf) phase Hf<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(tdc)<sub>5</sub>(Ac)<sub>2</sub>·9.3H<sub>2</sub>O·4.5DMF: Calcd C 21.38%, H 2.65%, N 2.36%, S 6.01%; Found C 21.21%, H 2.84%, N 2.53%, S 6.20%. Analytical data for thermally (120 °C) dry phase Hf<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(tdc)<sub>5</sub>(Ac)<sub>2</sub>·2.8H<sub>2</sub>O·0.4DMF: Calcd C 18.78%, H 1.27%, N 0.25%, S 7.12%; Found C 18.62%, H 1.43%, N 0.42%, S 7.24%.

**X-ray Crystallography.** All data sets were collected at Helmholtz Centre Berlin for Materials and Energy on beamline BESSY-MX BL-14.2, equipped with a Mar MX-225 CCD detector (Rayonics, Illinois).<sup>14</sup> The monochromatic radiation with  $\lambda = 0.88561 \text{ \AA}$  was used for the data collection. Images were recorded at room temperature using  $\varphi$ -scan technique with a scan width of 1° and an exposure time of 1.2 s/frame. Data sets were integrated and scaled with Mosflm 1.0.5<sup>15</sup> and Scala<sup>16</sup> software, respectively. Structures were solved by direct methods and refined in anisotropic approximation for all non hydrogen atoms by full-matrix least-squares on  $F^2$  using SHELXTL program package.<sup>17</sup> The hydrogen atoms were placed in geometrically calculated positions and refined using a “riding” model. After localization of all atoms belonging to the framework of both DUT-67 structures, relatively high peaks in the electron residual density map (3.37 and 3.16 e Å<sup>-3</sup> in the case of DUT-67(Zr) and 11.30 and 10.56 e Å<sup>-3</sup> in the case of DUT-67(Hf)) appear. The peaks are located at Wyckoff positions 24e and 48h and cannot be attributed to the disordered solvent molecules. The symmetry of the space group as well as the distances between the peaks (3.45–3.47 Å) point at disordered {Zr,Hf}<sub>6</sub>O<sub>6</sub>(OH)<sub>2</sub>(CH<sub>3</sub>COO)<sub>10</sub> cluster with small site occupancy factor (*sof*) (see ESI, Supporting Information Figure S2a). The refinement of *sof* for both positions gives occupancies 1.86 and 3.72%, respectively. It corresponds to 1.8 additional Zr<sub>6</sub>O<sub>8</sub>/Hf<sub>6</sub>O<sub>8</sub> cluster per unit cell (0.075 per formula unit). The encapsulated clusters are disordered over 4 positions in the center of 6 out of 10 cuboctahedral pores, located at 4a Wyckoff position.

During the refinement of both DUT-68(Zr) and DUT-68(Hf) structures, additional tdc<sup>2-</sup> linker molecule with site occupancy 0.25, disordered over 4 positions, because of the symmetry elements of the space group could be localized. After all framework atoms were refined anisotropically, several intensive electron density peaks were still present. The first three highest residual electron density peaks, generated by Fourier transformation amount to 4.50, 3.68, and 2.65 e Å<sup>-3</sup> for DUT-68(Zr) and 12.43, 8.92, and 3.63 e Å<sup>-3</sup> for DUT-68(Hf), located in 12e 4m.m (first two) and 96l (third one) Wyckoff positions. It results in two disordered octahedra after applying space group symmetry operations (Supporting Information Figure S2b). Refinement of the Zr atoms occupancy, assigned to the peaks, results in 0.75% for the first two peaks and 2.87% for the third one. It is equal to 4.2 additional Zr atoms or nearly 2/3 Zr<sub>6</sub>O<sub>8</sub> cluster per unit cell. In the case of DUT-68(Hf), the occupancies are refined to values 0.825% (first two peaks) and 4.0% (third one), resulting in 5.4 additional Hf atoms per unit cell. In crystal structures of DUT-69(Zr) and DUT-69(Hf), the positional disorder of 4 Hf atoms over 2 sites from the framework cluster has been treated with occupancies 0.77/0.23 and



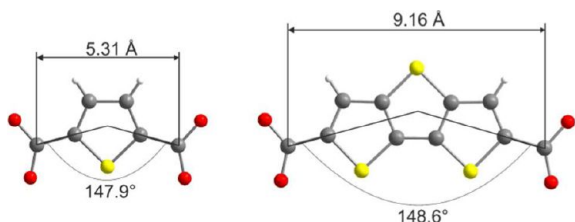
0.81/0.19 correspondingly. In order to locate the positions partially occupied by disordered metal clusters from the difference Fourier map, all structures were refined without performing the SQUEEZE procedure.

CCDC-902898, 902899, 902900, 902901, 902902, 902903, 921643, and 921644 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Crystal data for DUT-67(Zr)  $C_{24}H_8O_{32}S_4Zr_{6.45}$ :  $M_r = 1495.91$ , cubic  $Fm\bar{3}m$ ,  $a = 39.120(5)$  Å,  $V = 59868(12)$  Å<sup>3</sup>,  $Z = 24$ ,  $D_c = 1.015$  g cm<sup>-3</sup>, 3021 independent reflections observed,  $R_1 = 0.0705$  ( $I > 2\sigma(I)$ ),  $wR_2 = 0.2064$  (all data), and  $GOF = 1.104$ , residual electron density max/min 1.513/−2.614 e Å<sup>-3</sup>. Crystal data for DUT-67(Hf)  $C_{24}H_8Hf_{6.45}O_{32}S_4$ :  $M_r = 2087.14$ , cubic  $Fm\bar{3}m$ ,  $a = 39.010(5)$  Å,  $V = 59365(12)$  Å<sup>3</sup>,  $Z = 24$ ,  $D_c = 1.401$  g cm<sup>-3</sup>, 3085 independent reflections observed,  $R_1 = 0.0366$  ( $I > 2\sigma(I)$ ),  $wR_2 = 0.1246$  (all data), and  $GOF = 1.145$ , residual electron density max/min 1.705/−0.932 e Å<sup>-3</sup>. Crystal data for DUT-68(Zr)  $C_{26.40}H_{8.80}O_{32.60}S_{4.40}Zr_{6.07}$ :  $M_r = 1541.72$ , cubic  $Im\bar{3}m$ ,  $a = 53.680(6)$  Å,  $V = 154681(31)$  Å<sup>3</sup>,  $Z = 60$ ,  $D_c = 0.993$  g cm<sup>-3</sup>, 14841 independent reflections observed,  $R_1 = 0.0795$  ( $I > 2\sigma(I)$ ),  $wR_2 = 0.2403$  (all data), and  $GOF = 1.055$ , residual electron density max/min 2.655/−1.305 e Å<sup>-3</sup>. Crystal data for DUT-68(Hf)  $C_{26.40}H_{8.80}Hf_{6.09}O_{32.80}S_{4.40}$ :  $M_r = 2079.18$ , cubic  $Im\bar{3}m$ ,  $a = 53.510(6)$  Å,  $V = 153216(31)$  Å<sup>3</sup>,  $Z = 60$ ,  $D_c = 1.352$  g cm<sup>-3</sup>, 14690 independent reflections observed,  $R_1 = 0.0611$  ( $I > 2\sigma(I)$ ),  $wR_2 = 0.1891$  (all data), and  $GOF = 1.062$ , residual electron density max/min 2.480/−2.739 e Å<sup>-3</sup>. Crystal data for DUT-69(Zr)  $C_{30}H_{10}O_{32}S_5Zr_6$ :  $M_r = 1590.00$ , orthorhombic  $P2_12_12_1$ ,  $a = 13.570(3)$  Å,  $b = 19.800(4)$  Å,  $c = 28.390(6)$  Å,  $V = 7628(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.385$  g cm<sup>-3</sup>, 6802 independent reflections observed,  $R_1 = 0.0888$  ( $I > 2\sigma(I)$ ),  $wR_2 = 0.2771$  (all data), and  $GOF = 1.082$ , residual electron density max/min 2.610/−2.007 e Å<sup>-3</sup>. Crystal data for DUT-69(Hf)  $C_{30}H_{10}Hf_6O_{32}S_5$ :  $M_r = 2113.62$ , orthorhombic  $P2_12_12_1$ ,  $a = 13.530(3)$  Å,  $b = 19.710(4)$  Å,  $c = 28.300(6)$  Å,  $V = 7547(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.860$  g cm<sup>-3</sup>, 8741 independent reflections observed,  $R_1 = 0.0524$  ( $I > 2\sigma(I)$ ),  $wR_2 = 0.1517$  (all data), and  $GOF = 1.120$ , residual electron density max/min 2.482/−1.952 e Å<sup>-3</sup>. Crystal data for DUT-67(Zr), treated with conc.  $CH_3COOH$  for 1 week  $C_{24}H_8O_{32}S_4Zr_6$ :  $M_r = 1483.86$ , cubic  $Fm\bar{3}m$ ,  $a = 39.110(5)$  Å,  $V = 59822(12)$  Å<sup>3</sup>,  $Z = 24$ ,  $D_c = 0.989$  g cm<sup>-3</sup>, 3043 independent reflections observed,  $R_1 = 0.0642$  ( $I > 2\sigma(I)$ ),  $wR_2 = 0.2186$  (all data), and  $GOF = 1.076$ , residual electron density max/min 3.631/−1.285 e Å<sup>-3</sup>. Crystal data for DUT-67(Zr), soaked in water for 1 week  $C_{24}H_8O_{32}S_4Zr_6$ :  $M_r = 1483.86$ , cubic  $Fm\bar{3}m$ ,  $a = 39.030(5)$  Å,  $V = 59456(12)$  Å<sup>3</sup>,  $Z = 24$ ,  $D_c = 0.995$  g cm<sup>-3</sup>, 3080 independent reflections observed,  $R_1 = 0.0666$  ( $I > 2\sigma(I)$ ),  $wR_2 = 0.2289$  (all data), and  $GOF = 1.094$ , residual electron density max/min 1.766/−0.784 e Å<sup>-3</sup>.

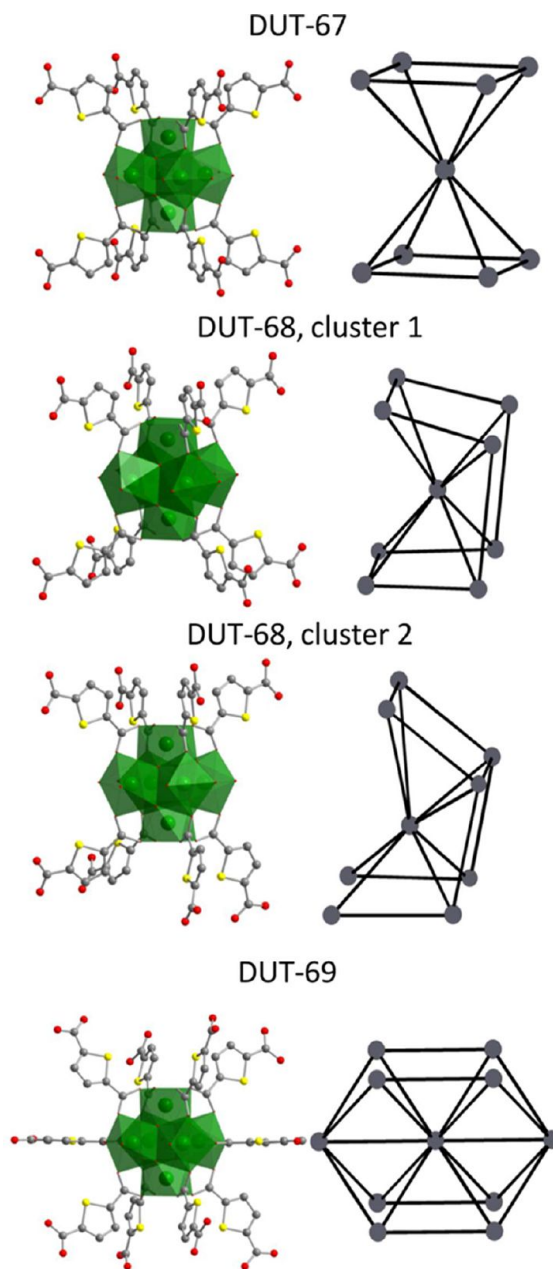
## RESULTS AND DISCUSSION

**Synthesis and structures.** The ligand  $H_2tdc$  has the same angle between terminal carboxylates as  $H_2dttc$  ( $H_2dttc$  =



**Figure 1.** Geometry of the linkers:  $tdc^{2-}$  (left) and  $dttc^{2-}$  (right).

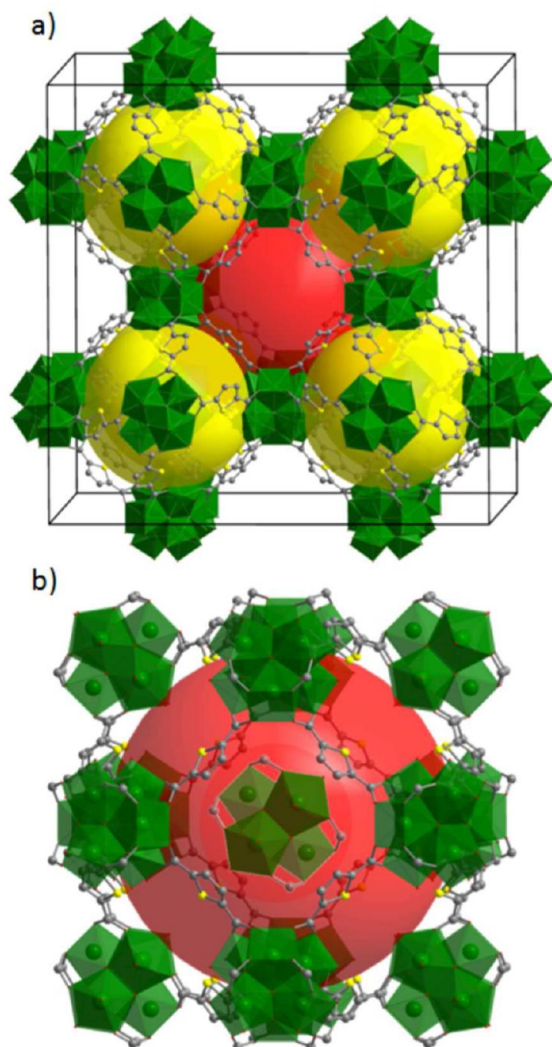
dithieno[3,2-*b*;2',3'-*d'*]thiophene-2,6-dicarboxylate), used earlier for DUT-51 synthesis, and therefore, it can be considered as a shortened version of the latter (Figure 1).



**Figure 2.** Linker orientation in the cluster (left) and local environment of Zr/Hf clusters (right) in DUT-67, DUT-68, and DUT-69 structures from the topological point of view (gray circles symbolize the clusters and the edges correspond to the  $tdc^{2-}$  ligands).

Hence, a compound isorecticular to DUT-51 was expected as a product of the reaction between  $H_2tdc$  and  $Zr^{4+}$  salt. Indeed, the reaction between zirconium or hafnium chloride and  $H_2tdc$  in the mixture of DMF and NMP (1:1) as solvent at 120 °C in the presence of 120 equivalents of acetic acid (modulator) yields DUT-67 with framework composition  $[Zr_6O_6(OH)_2(tdc)_4(CH_3COO)_2]$  for DUT-67(Zr) and  $[Hf_6O_6(OH)_2(tdc)_4(CH_3COO)_2]$  for DUT-67(Hf). The acetic acid was chosen as a modulator, because the benzoic acid (successfully used in DUT-51 synthesis) seems to be too bulky to be bound by the cluster simultaneously with  $tdc^{2-}$  and does not lead to the product formation at all.

Single-crystal X-ray diffraction analysis confirms isorectularity of DUT-67 with DUT-51.<sup>12</sup> The new compound

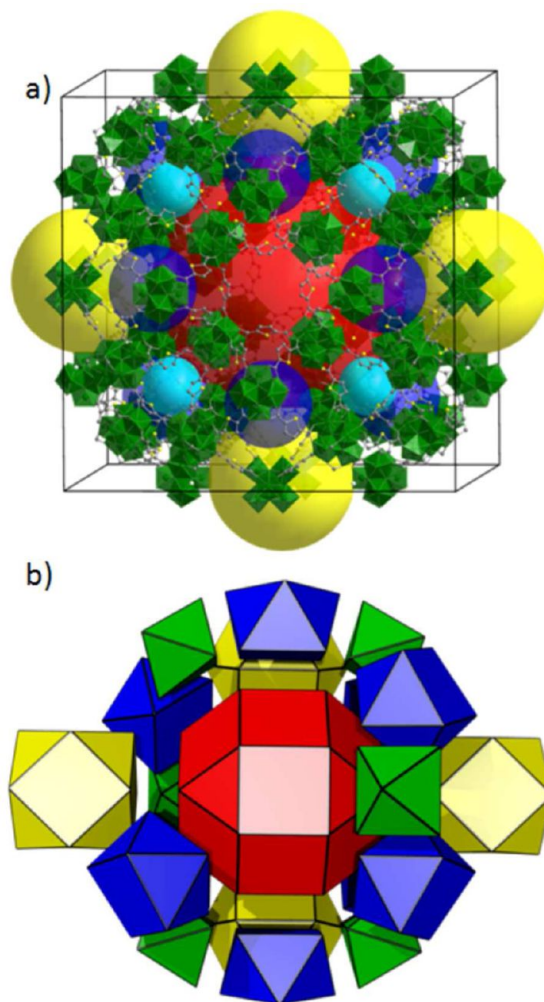


**Figure 3.** (a) Packing diagram with pores location (red sphere, cuboctahedral pore; yellow spheres, octahedral pores) and (b)  $\{Zr,Hf\}_6O_6(OH)_2(CH_3COO)_{10}$  cluster inside the cuboctahedral pore (disorder neglected).

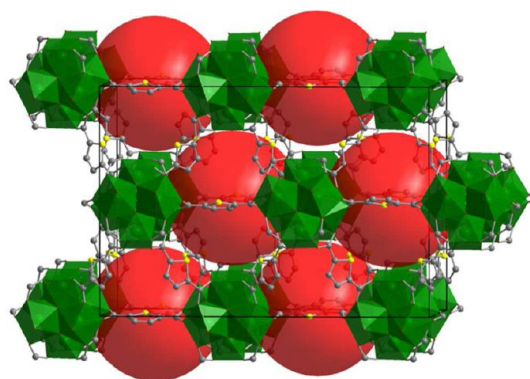
crystallizes in  $Fm\bar{3}m$  space group with  $a = 39.120(5)$  Å, which is significantly smaller than that of DUT-51 ( $a = 49.964(6)$  Å). This causes decreasing of inner pores diameters from 18.8 Å for cuboctahedral and 15.6 Å for octahedral cage in the case of DUT-51 to 14.2 Å and 11.7 Å in DUT-67, respectively (Figure 3a). The structure of DUT-67, similar to DUT-51, contains an 8-connected cluster (Figure 2).

During refinement of DUT-67(Zr) and DUT-67(Hf) crystal structure, the additional disordered  $M_6$  based cluster (M—Zr, Hf) with minor occupancy (Supporting Information Figure S2a) has been localized in the center of cuboctahedral pore (see experimental part and ESI for more details).

The distance, measured from the zirconium atom of the framework (coordinated by the modulator) to the nearest metal atom of the encapsulated cluster is 9.7 Å, giving us an idea, that the encapsulated cluster, located in the center of the cuboctahedral pore can be bonded to the framework by additional  $tdc^{2-}$  linker molecules (Zr—Zr distance between  $tdc^{2-}$  connected atoms inside the framework is 9.6 Å), which because of disorder, low occupancy, and high symmetry could not be located from the difference Fourier map. The situation,



**Figure 4.** (a) A fragment of the framework showing the pores in DUT-68 and (b) representation of the pore shapes in DUT-68 as natural tiles.

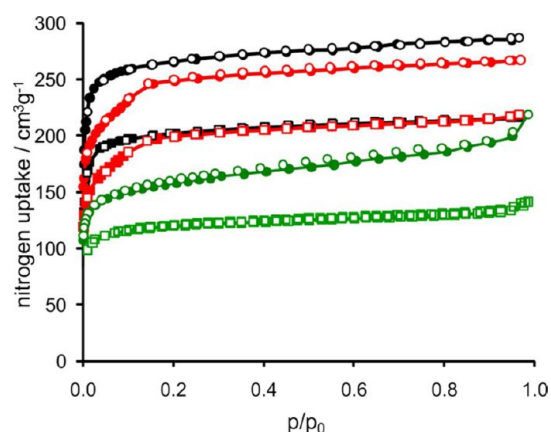


**Figure 5.** Representation of the pore packing in DUT-69.

that the encapsulated clusters are different in coordination and have a composition  $Zr_6O_6(OH)_2(CH_3COO)_{10-0.5x}(tdc)_{0.5x}(solv)_4$  ( $1 < x < 10$ ) is also possible.

To prove this finding, additional X-ray single crystal diffraction experiments were performed with DUT-67(Zr) crystals, soaked in concentrated  $CH_3COOH$  or water for 1 week. As a result, in case of acetic acid, the same electron

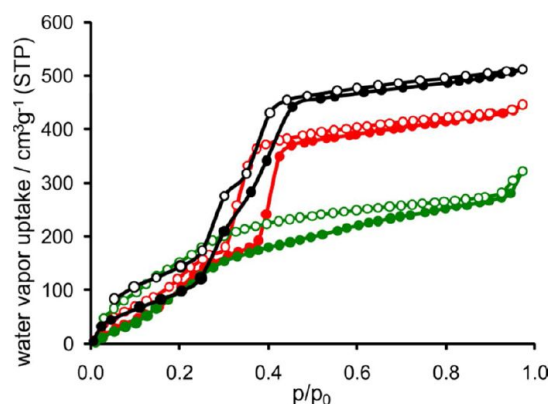




**Figure 6.** Nitrogen adsorption (solid symbols) and desorption (open symbols) isotherms at 77 K: circles, zirconium-based MOFs; squares, hafnium-based MOFs; black, DUT-67; red, DUT-68; green, DUT-69.

**Table 1.** Textural Properties of Investigated MOFs

	DUT-67	DUT-68	DUT-69
zirconium MOFs			
BET calcd ( $\text{m}^2\text{g}^{-1}$ )	1767	1786	1110
BET exp. ( $\text{m}^2\text{g}^{-1}$ )	1064	891	560
V pore ( $\text{cm}^3\text{g}^{-1}$ )	0.44	0.41	0.31
hafnium MOFs			
BET calcd ( $\text{m}^2\text{g}^{-1}$ )	1221	1299	843
BET exp. ( $\text{m}^2\text{g}^{-1}$ )	810	749	450
V pore ( $\text{cm}^3\text{g}^{-1}$ )	0.33	0.34	0.22

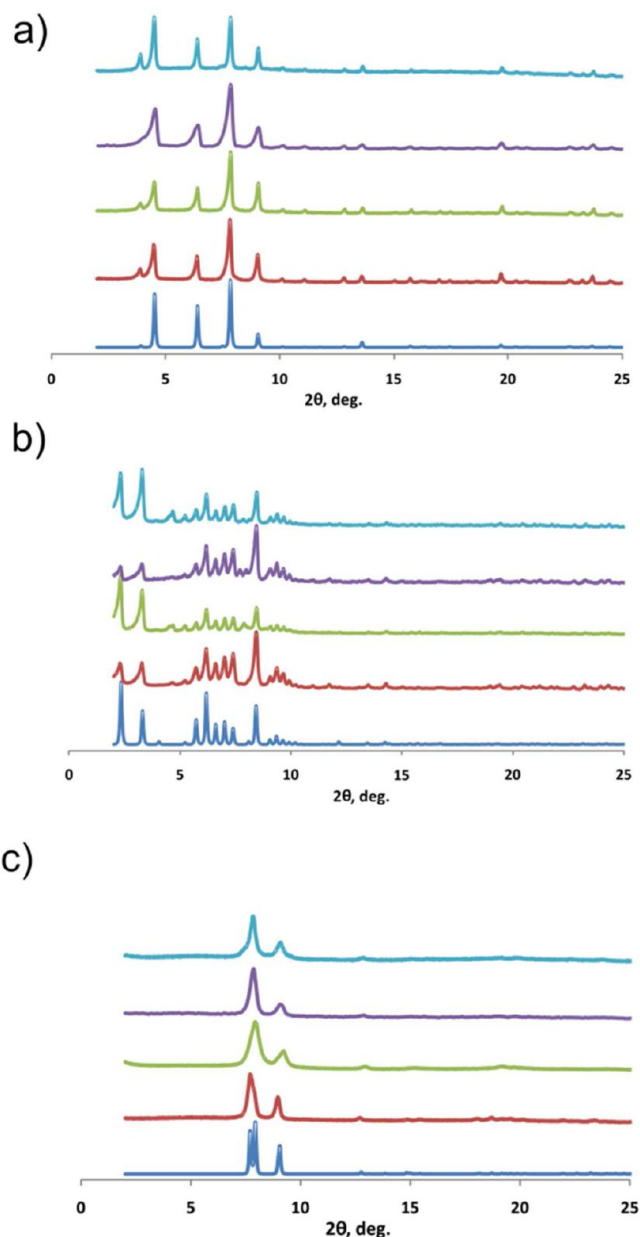


**Figure 7.** Water vapor adsorption (solid symbols) and desorption (open symbols) isotherms at 298 K of zirconium-based MOFs: black, DUT-67; red, DUT-68; green, DUT-69.

density like in case of as-made phase was found in difference Fourier map at the final stage of structure refinement. On the contrary, the structure refinement of the crystal soaked in water, results in the absence of electron density in the pore center, and two times lower residual electron density, located in the other positions of the unit cell. This finding supports an idea, that the incorporated clusters can be removed by the hydrolysis in water.

Two further polymorphs to DUT-67 (in accordance to powder XRD experiments) were obtained by varying amount of modulator during the synthesis.

Utilization of 180 equiv of acetic acid leads to the formation of cubic shaped crystals of DUT-68(Zr) and DUT-68(Hf) with frameworks composition  $\{\text{Zr,Hf}\}_6\text{O}_6(\text{OH})_2(\text{tdc})_{4.5}(\text{Ac})$  (Sup-



**Figure 8.** Powder XRD patterns: (a) DUT-67(Zr), (b) DUT-68(Zr), (c) DUT-69(Zr). (Color codes: blue line, calculated powder diffraction pattern; red, as-synthesized; green, thermally dried; violet, soaked in water for 24 h; navy blue, soaked in conc. HCl for 3 days in case of DUT-67 and DUT-68 and HCl (1 mol/L) for 1 day for DUT-69).

porting Information Figure S1, ESI), crystallizing in  $Im\bar{3}m$ . The structure involves two crystallographically independent 8-connected clusters  $\{\text{Zr,Hf}\}_6\text{O}_6(\text{OH})_2$  (Figure 2) giving rise to a *binodal* 8-connected net unprecedented so far in structural chemistry (see below a more detailed discussion).

The complicated hierarchical pore architecture of DUT-68 consist of 4 types of pores (Figure 4a): rhombicuboctahedral mesopore with inner diameter of 27.7 Å, cuboctahedral cage with 13.9 Å in diameter, square antiprismatic pore with 12.5 Å in size, and smallest octahedral pores with 8 Å in diameter of the inner sphere (vdW radii of atoms were taken into account).

The largest rhombicuboctahedral mesopore is located in the center of the unit cell and share its square windows with six

cuboctahedral cages along three crystallographic axes (Figure 4b). Remaining square windows of the rhombicuboctahedral pore are shared with 12 square antiprismatic cages. Octahedral pores are formed as a result of stacking of 6 square antiprisms and 2 rhombicuboctahedral mesopores.

During the refinement of DUT-68 crystal structures, the observation similar to that for DUT-67 was made: additional Zr- or Hf-based clusters are incorporated in the pores of the framework. These clusters, positioned in the rhombicuboctahedral pore, are disordered by symmetry over 6 positions. Besides disordered clusters, one additional  $\text{tdc}^{2-}$  linker disordered over 4 positions by symmetry could be located from the difference Fourier map. It results in the SBU/linker ratio of 1:4.4 in the incorporated clusters (the SBU/linker ratio for the framework itself is 1:4), which is in accordance with elemental analysis and TG data, provided the ratio 1:4.5.

If the acetic acid amount was decreased to 50 equivalents instead of 120 during the synthesis, DUT-69(Zr) and DUT-69(Hf) materials with frameworks composition  $\{\text{Zr,Hf}\}_6\text{O}_4(\text{OH})_4(\text{tdc})_5(\text{Ac})_2$  were obtained. The structure of DUT-69 is based on the *uninodal* 10-connected framework with the **bct** topology, and is thus the first Zr/Hf-based MOF involving 10-connected SBU (Figure 2). Such a cluster implies 4 additional, other than  $\text{tdc}^{2-}$ , ligands. The single crystal diffraction data allowed us to determine only the positions of oxygen atoms of these ligands, hence the elemental, as well as thermogravimetric analysis were performed to determine the overall cluster composition. Accordingly, two acetates and 2 water molecules act as additional ligands resulting in the composition  $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{tdc})_5(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$ .

The **bct** topology involves octahedral cages, where the sphere with the diameter of 5 Å can be inscribed (Figure 5). The rectangular channels  $9.15 \times 2.66$  Å in size are running along the *c* crystallographic axis.

To rationalize framework topologies realized in DUT-67, DUT-68, and DUT-69, it is helpful to consider the connections between Zr-clusters (Figure 2). In the original UiO-66 structure Zr-octahedra are linked together through all their edges by twelve dicarboxylates that predetermines the topology of 12-coordinated **fcu** net.<sup>18–20</sup> The networks **reo** and **bct** found in DUT-67 and DUT-69, respectively, are simply related to **fcu** if four or, respectively, two vertices of the parent cuboctahedron are omitted (Supporting Information Figure S3). On the contrary, an unexpected, new *binodal* 8-coordinated net that is not directly related to **fcu** is observed in DUT-68. The nodes of the net correspond to the two independent clusters having  $\bar{4}m.2$  (cluster 1) and  $\dots m$  (cluster 2) site symmetry, respectively. At the same time, the clusters in this *binodal* net have environment close to that in the **reo** net, but an apparent “switch” of the two connections from the square bases to the axial positions (see Figure 2) induces a change in the topology.

From the crystal engineering point of view, it is interesting to target the formation of the most symmetric 8-coordinated net **bcu**, that of the body-centered cubic lattice. In the case of DUT-67–69 structures the **bcu** net cannot be realized since Zr-clusters are linked via their edges. If the octahedral Zr-clusters were linked via faces rather than via edges, then the **bcu** net would be the default topology [analogously, the default topology of vertex-connected octahedra is that of the primitive cubic lattice (**pcu**)]. However, the design of a chelating ligand capable to simultaneously bind six Zr atoms belonging to the two triangular faces of neighboring octahedra definitely represents a challenge. At the same time, the formation of a

capped Zr-octahedron (similar to, e.g.,  $[\text{Re}_6\text{S}_8(\text{OH})_6]^{4-}$  cluster) could facilitate to achieve the **bcu** arrangement.

**Porosity and Adsorption Experiments.** The thermal stability of DUT-67, DUT-68, and DUT-69 materials (up to 300 °C) (Supporting Information Figure S6–S13) is significantly higher in comparison to DUT-51 (150 °C) but is lower in comparison to UiO-66 (500 °C).

The solvent accessible void volume of the DUT-67, DUT-68 (the encapsulated clusters were omitted), and DUT-69 amounts to 66.1%, 60.2%, and 50.9%, respectively.<sup>21</sup>

The specific surface area, calculated geometrically using the program Poreblazer,<sup>22</sup> is 1767  $\text{m}^2 \text{g}^{-1}$  for DUT-67(Zr) and 1221  $\text{m}^2 \text{g}^{-1}$  for DUT-67(Hf), 1786 for DUT-68(Zr) and 1299  $\text{m}^2 \text{g}^{-1}$  for DUT-68(Hf) (encapsulated clusters are omitted), 1110  $\text{m}^2 \text{g}^{-1}$  for DUT-69(Zr) and 843  $\text{m}^2 \text{g}^{-1}$  for DUT-69(Hf).

Nitrogen physisorption experiments at 77 K up to 1 bar revealed “Type I” isotherms with maximum nitrogen uptake of 287  $\text{cm}^3 \text{g}^{-1}$  for DUT-67(Zr) and 216  $\text{cm}^3 \text{g}^{-1}$  for DUT-67(Hf) (Figure 6). The specific surface area, calculated using multipoint BET theory (in the relative pressure range  $3 \times 10^{-3}$  to  $5 \times 10^{-2} p/p_0$ ) amounts only to 1064 and 810  $\text{m}^2 \text{g}^{-1}$  for DUT-67(Zr) and DUT-67(Hf), respectively, confirming the possible partial pore blocking by additional cluster incorporated in the compounds. The corresponding specific pore volume is 0.44  $\text{cm}^3 \text{g}^{-1}$  for DUT-67(Zr) and 0.33  $\text{cm}^3 \text{g}^{-1}$  for DUT-67(Hf).

Nitrogen adsorption experiments of both DUT-68 materials result in isotherms with more flat slope (Figure 6) confirming accessibility of the mesoporous cages. Using multipoint BET approach in the relative pressure range of  $4 \times 10^{-2}$ – $1 \times 10^{-1}$ , specific surface areas for DUT-68(Zr) and DUT-68(Hf) are calculated to be 891  $\text{m}^2 \text{g}^{-1}$  and 749  $\text{m}^2 \text{g}^{-1}$ , respectively. The corresponding pore volume is 0.41  $\text{cm}^3 \text{g}^{-1}$  for zirconium-based MOF and 0.34  $\text{cm}^3 \text{g}^{-1}$  for hafnium-containing compound.

The nitrogen physisorption isotherms of thermally dried DUT-69(Zr) and DUT-69(Hf) correspond to “type I”, typical for microporous materials with a slightly increasing uptake at higher relative pressure indicating the presence of nanosized crystallites in the sample and multilayer adsorption on the external surface (Figure 6).

The corresponding BET specific surface areas are 560 and 450  $\text{m}^2 \text{g}^{-1}$  for DUT-69(Zr) and DUT-69(Hf) if multipoint approach is used for calculation in the relative pressure ranges  $4 \times 10^{-3}$ – $5 \times 10^{-2}$  for DUT-69(Zr). The pore volume calculated at 0.9  $p/p_0$  are 0.31 and 0.20  $\text{cm}^3 \text{g}^{-1}$  for DUT-69(Zr) and DUT-69(Hf), respectively. The textural properties of investigated compounds are summarized in Table 1.

The water physisorption isotherms provide useful information regarding the hydrophilic/hydrophobic properties of the compounds and allow to estimate the pore filling degree of the MOFs at high humidity level. Interestingly, the DUT-67 materials, which are isorecticular to DUT-51 have significantly more hydrophilic surface in comparison to DUT-51. The adsorption at 298K starts already at low relative pressure (Figure 7, Supporting Information Figure S14). The specific pore volume estimated from water adsorption isotherm is also in good agreement with the pore volume calculated from nitrogen adsorption isotherm and is 0.41  $\text{cm}^3 \text{g}^{-1}$  for DUT-67(Zr), 0.36  $\text{cm}^3 \text{g}^{-1}$  for DUT-68(Zr), and 0.26  $\text{cm}^3 \text{g}^{-1}$  for DUT-69(Zr). Also the different pore size distributions of investigated MOFs are reflected in water adsorption isotherms. The truly microporous DUT-69 shows continuously increasing uptake. In contrast, the isotherms of DUT-68 and DUT-67

exhibits steps, indicating the successive filling of pores with different size.

**Chemical and Thermal Stability.** Hydrolytical stability of materials was evaluated by soaking of dried powders in water for 24 h, as well as by repeated water adsorption isotherms. As it can be seen in Figure 8, the soaking in water does not cause changes in powder diffraction patterns pointing on the intact structure. The chemical stability of DUT-67, DUT-68, and DUT-69 materials toward acidic and basic conditions was evaluated by immersing dried powders in the concentrated HCl and NaOH with the concentration 1 mol/L for 3 days. The integrity of frameworks was proven by XRD experiments (Figure 8, Supporting Information Figure S4–S5). As a result, DUT-67 and DUT-68 remain unchanged in the strong acidic medium, but by the DUT-69(Zr) the decomposition occurs. Although, DUT-69(Zr) is stable for 1 day in less concentrated HCl ( $c = 1$  mol/L), as it can be seen from XRPD patterns. The exposure of investigated MOFs to basic conditions causes the decomposition of all materials.

## SUMMARY AND CONCLUSIONS

Summarizing, we have made the following findings in the Zr/Hf MOFs chemistry by using the combination of the bent linker and modulator synthesis approach: (i) in the absence of a modulator only amorphous products are formed; (ii) changing the modulator concentration or using solvent mixtures lead to the polymorphic MOF materials with different framework topologies and pore systems (from **bct** topology in DUT-69 with pore diameter 5 Å over **reo** topology in DUT-67 having a largest pore of 14.2 Å to 8,8-connected framework in DUT-68 with 27.7 Å mesopore); (iii) by using high modulator concentration, the partial encapsulation of the  $\{Zr,Hf\}_6O_6(OH)_2(CH_3COO)_{10}(solv)_4$  clusters into pores takes place (the cluster acts to some extent as a template).

All synthesized compounds are robust, chemically, and thermally stable up to 300 °C. Specific surface areas calculated from nitrogen adsorption isotherms measured at 77 K amount to 1064 m<sup>2</sup> g<sup>−1</sup> for DUT-67(Zr), 891 m<sup>2</sup> g<sup>−1</sup> for DUT-68(Zr), and 560 m<sup>2</sup> g<sup>−1</sup> for DUT-69(Zr). Specific surface areas of corresponding Hf analogues are lower because of the higher density of frameworks.

## ASSOCIATED CONTENT

### Supporting Information

Details of single-crystal X-ray diffraction analysis, powder X-ray diffractograms, thermogravimetric analysis, and additional physisorption data. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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All authors contributed equally to this work.

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### Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

MOFs, metal–organic frameworks; UiO, Universitet i Oslo; DTTDC, dithieno[3,2-*b*;2',3'-*d*]thiophene-2,6-dicarboxylate; DUT, Dresden University of Technology; SBU, Secondary Building Unit; DMF, *N,N'*-dimethylformamide; NMP, *N*-methyl-2-pyrrolidone; Ac, acetate; BET, Brunauer–Emmett–Teller; XRPD, X-ray powder diffraction

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