

A highly porous flexible Metal–Organic Framework with corundum topology†‡

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A flexible Metal–Organic Framework $Zn_4O(\text{BenzTB})_{3/2}$ (DUT-13) was obtained by combination of a tetratopic linker and Zn_4O^{6+} as connector. The material has a corundum topology and shows the highest pore volume among flexible MOFs.

In the last two decades a new class of materials, namely Metal–Organic Frameworks (MOFs), has set records concerning high specific surface area and pore volume.^{1–4} Compared to other porous materials like zeolites, mesoporous oxides or activated carbons, MOFs of the so called 3rd generation have flexible structures.⁵ The structural changes are often induced by guest molecules acting as external stimuli. Therefore those compounds are promising candidates for applications in gas separation,^{6,7} as drug delivery agents⁸ or sensors.⁹ A number of representatives for this generation have been reported. Regarding their topology they can be grouped into the following categories: interdigitated 2D-layer structures like $\text{Cu}(\text{dhbc})_2(\text{bpy})$,¹⁰ $\text{Cd}(\text{bpndc})(\text{bpy})$ ¹¹ and $\text{Zn}_2(\text{ip})_2(\text{bpy})_2$,¹² pillared-layer compounds like $\text{M}_2(\text{L})_2(\text{dabco})$ ($\text{M} = \text{Zn}, \text{Ni}, \text{Cu}$; $\text{L} = 1,4\text{-bdc}, 2,6\text{-ndc}$)¹³ or $\text{Cu}_2(\text{pzdc})_2(\text{dpyg})$,¹⁴ coordination polymers with channel systems like $\text{Ag}_3(\text{atz})_2$ ¹⁵ and the MIL-53 series,¹⁶ or interpenetrated compounds with moving networks caused by π,π -stackings of the linker molecules.^{7,17,18} The compounds show distinguished flexibility, the so called “gate-pressure” effect. That means that the pore system shrinks or expands at a certain loading of guest molecules at given conditions.

Recently we reported a series of compounds based on the tetratopic N,N,N',N' -benzidinetetrabenzoate (BenzTB^{4-}) linker and paddle-wheel units (DUT-10/11/12, DUT = Dresden University of Technology), which show interesting fluorescence and selective gas adsorption properties. The compounds show an irreversible transformation during the desolvation procedure by shrinkage of the pore system. In this case the pore narrowing causes the selective gas adsorption properties.¹⁸ Furthermore, a doubly-interpenetrated magnesium contained framework (SNU-25) with selective gas adsorption properties was synthesized by Suh *et al.* using BenzTB^{4-} as ligand.¹⁹

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Herein, we report the synthesis and characterization of a new microporous Metal–Organic Framework, $\text{Zn}_4\text{O}(\text{BenzTB})_{3/2}$ (DUT-13), based on the same linker but with exceptional high pore volume and a “reverse type” of flexibility: framework opening effect caused by adsorption of N_2 (at -196°C), CO_2 (at -78°C) and $n\text{-C}_4\text{H}_{10}$ (at 20°C).

The N,N,N',N' -benzidinetetrabenzoic acid (H_4BenzTB) was synthesized as described earlier (see ESI†).¹⁸ Single crystals of $\text{Zn}_4\text{O}(\text{BenzTB})_{3/2}$ suitable for X-ray diffraction analysis were obtained by solvothermal reaction of H_4BenzTB and zinc nitrate in N,N -diethylformamide (DEF) and glacial acetic acid as additive.† The compound crystallizes in the trigonal space group $R\bar{3}c$ and shows a corundum topology (**cor**). The structure is built up by $\text{Zn}_4\text{O}(\text{O}_2\text{C})_6$ as Secondary Building Unit (SBU) and presents two different types of pores. The main larger pore centered at Wyckoff positions 6b ($0,0,0$) with C_{3i} symmetry is constructed by eight Zn_4O^{6+} clusters that are arranged in hexagonal bipyramidal geometry and connected by six BenzTB^{4-} ligands. The dimension of this pore is $14.7 \times 9.5 \text{ \AA}$ in diameter (van der Waals radii of corresponding atoms have been considered). The solvent-accessible volume calculated with PLATON²⁰ is $53\,995 \text{ \AA}^3$ corresponding to 82.4% of the unit cell volume. The pores form a rhombohedrally distorted cubic close packing (*ccp*) (Fig. S2, ESI†).

Smaller pores (not detected by PLATON) with $6.8 \times 5.0 \text{ \AA}$ in diameter are placed in the pseudo-octahedral holes of *ccp* (Fig. 1). They are formed by two Zn_4O^{6+} clusters and three linker molecules. To the best of our knowledge DUT-13 is the first MOF with a complex pore system typical for rigid MOFs and a flexible framework (“gate-pressure” properties).

To study the porosity of DUT-13, the nitrogen physisorption measurement was performed at -196°C . For this purpose the

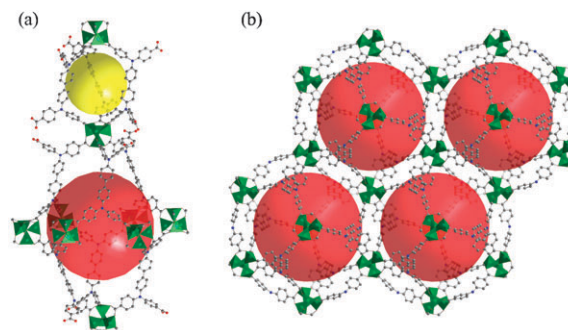


Fig. 1 Crystal structure of DUT-13 (a) the large hexagonal bipyramidal (red) and the small (yellow) pore; (b) arrangement of the large pores in a plane vertically along $[0\ 0\ 1]$ in a *ccp* motif (red and yellow spheres indicate pore volume).

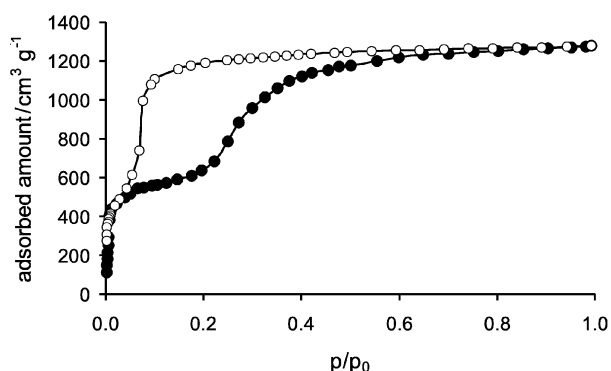


Fig. 2 N_2 adsorption/desorption (\bullet / \circ) isotherms of DUT-13 (-196°C).

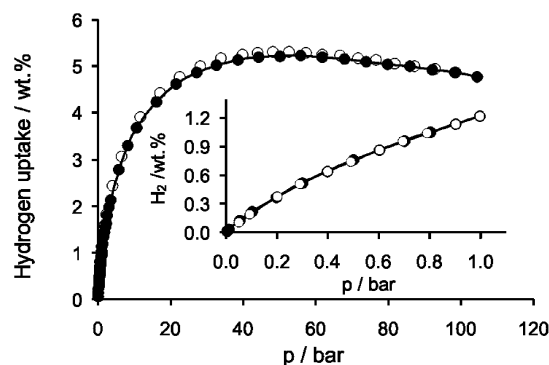


Fig. 3 High pressure excess hydrogen (-196°C) adsorption (\bullet) and desorption (\circ) of DUT-13; inset: low pressure region up to 1 bar (-196°C).

synthesized material was washed with DEF, followed by an exchange of the solvent with absolute ethanol, and finally dried using a supercritical carbon dioxide technique.²¹ The nitrogen physisorption measurement reveals two steps in the adsorption branch of the isotherm (Fig. 2 and Fig. S3, ESI \ddagger). Up to a relative pressure of 0.15 the observed isotherm corresponds to a classical type I isotherm reaching the plateau at about $600\text{ cm}^3\text{ g}^{-1}$. At a pressure of $0.2 p/p_0$ (so called gate-opening pressure), a sudden rise in the isotherm occurs. The isotherm reaches saturation at $1279\text{ cm}^3\text{ g}^{-1}$. The total pore volume estimated at $p/p_0 = 0.99$ is $1.98\text{ cm}^3\text{ g}^{-1}$ and therefore the highest value for flexible MOFs observed so far and among the highest values reported for MOFs (MOF-177: N_2 saturation uptake (SU): $1350\text{ cm}^3\text{ g}^{-1}$, pore volume (V_p): $1.59\text{ cm}^3\text{ g}^{-1}$;¹ UMCM-2: SU: $1500\text{ cm}^3\text{ g}^{-1}$, V_p : $2.02\text{ cm}^3\text{ g}^{-1}$;⁴ DUT-6: SU: $1380\text{ cm}^3\text{ g}^{-1}$, V_p : $2.02\text{ cm}^3\text{ g}^{-1}$;³ PCN-68: V_p : $2.13\text{ cm}^3\text{ g}^{-1}$).²² The desorption branch does not trace the adsorption branch forming a hysteresis loop which closes at relative pressure of 0.02 (gate-closing pressure). At lower pressures ($p/p_0 \leq 0.01$) a second smaller hysteresis is obtained. Several reruns of the N_2 adsorption experiment using the same sample show a smaller hysteresis loop ending up in a type I like isotherm (see Fig. S4, ESI \ddagger) with a maximum amount adsorbed of $524\text{ cm}^3\text{ g}^{-1}$. Powder X-ray diffraction (PXRD) experiments after N_2 adsorption indicate changes of the structure of DUT-13 (Fig. S10, ESI \ddagger). The comparison of PXRD patterns after the first and third adsorption cycle reveals the partial

conversion of the framework (or maybe conversion of the part of crystallites) into another phase during the first adsorption cycle and further transformation in the following cycles.

The physisorption isotherm of *n*-butane measured at 20°C under atmospheric pressure and dynamic conditions (*n*-butane diluted with nitrogen) is shown in Fig. S6, ESI \ddagger . At 15% *n*-butane by volume a first plateau in the isotherm with a storage capacity of 0.36 g g^{-1} is reached. Higher *n*-butane concentrations (40 to 80% *n*-butane by volume) lead to a further increase of the adsorption capacity to 0.76 g g^{-1} . As shown for the nitrogen adsorption at -196°C the desorption branch reveals a different inflection in comparison to the adsorption branch. A hysteresis loop is observed which closes at 8% *n*-butane by volume whereas the first plateau of the adsorption was almost reached. Even for lower concentrations (8 to 0% *n*-butane by volume) the branches are shifted. Similar to the nitrogen adsorption, the second and third run of the physisorption performed on the same sample does not match the first measurement with a decrease of the total adsorption capacity to 0.38 g g^{-1} at the third run (Fig. S7, ESI \ddagger).

Interestingly, the adsorption of supercritical gases like hydrogen and methane at high pressures does not induce the gate opening (Fig. 3, Fig. S8, ESI \ddagger) and has no influence on the crystal structure of DUT-13 as confirmed by PXRD analysis (Fig. S10, ESI \ddagger). \ddagger The volumetric hydrogen adsorption measurement for DUT-13 reveals a maximum excess hydrogen storage capacity of $613\text{ cm}^3\text{ g}^{-1}$ at 56 bar and -196°C equal to 55 mg g^{-1} (5.23 wt%). With these values DUT-13 is ranking among the best MOFs for hydrogen storage (MOF-177: 75 mg g^{-1} at 60 bar,²³ PCN-68: 73 mg g^{-1} at 50 bar,²² DUT-6: 60 mg g^{-1} at 50 bar and -196°C).³

For applications such as natural gas storage, the methane physisorption isotherm was measured by use of a magnetic suspension balance at 25°C up to 150 bar (Fig. S8, ESI \ddagger). At 35 bar the excess uptake of DUT-13 is 131 mg g^{-1} ($71\text{ cm}^3\text{ cm}^{-3}$ based on the crystallographic density). The maximum gravimetric amount of methane adsorbed is 198 mg g^{-1} at 90 bar equal to $107\text{ cm}^3\text{ cm}^{-3}$. With these values DUT-13 is comparable to some of the best methane storage materials such as MIL-101 (239 mg g^{-1} at 125 bar),²⁴ DUT-6 (230 mg g^{-1} at 100 bar)³ and COF-102 (243 mg g^{-1} at 85 bar)²⁵ in terms of gravimetric values.

Because of its property as a greenhouse gas, the removal of CO_2 from exhaust gas is of increasing interest for industrial applications. At -78°C DUT-13 stores up to $379\text{ cm}^3\text{ g}^{-1}$ up to 1 bar (Fig. S9, ESI \ddagger). Just as for nitrogen and *n*-butane a hysteresis in the desorption branch was observed. PXRD measurements show a structural change similar to that during N_2 physisorption (Fig. S10, ESI \ddagger). N_2 physisorption after CO_2 adsorption indicates that this material still has a high residual porosity up to $2532\text{ m}^2\text{ g}^{-1}$ ($\text{BET } 0.007 \leq p/p_0 \leq 0.1$) with a saturation N_2 uptake of $769\text{ cm}^3\text{ g}^{-1}$ and a typical type I isotherm (Fig. S5, ESI \ddagger).

In conclusion, utilizing the tetracarboxylic acid H_4BenzTB as linker we synthesized and characterized a new highly porous Metal-Organic Framework $\text{Zn}_4\text{O}(\text{BenzTB})_{3/2}$ (DUT-13), showing flexibility as response to adsorption of certain gases. The MOF has a rare corundum topology not typical for flexible MOFs known so far. Physisorption measurements

revealed high storage capabilities of DUT-13 for nitrogen ($1279 \text{ cm}^3 \text{ g}^{-1}$), hydrogen ($613 \text{ cm}^3 \text{ g}^{-1}$, 5.23 wt% at 56 bar) and *n*-butane (0.76 g g^{-1}).

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Notes and references

§ Abbreviations: bpy = 4,4'-bipyridine, dhbc = 2,5-dihydroxybenzenedicarboxylate, bpndc = benzophenone-4,4'-dicarboxylate, ip = isophthalate, 1,4-bdc = 1,4-benzenedicarboxylate, 2,6-ndc = 2,6-naphthalenedicarboxylate, dabco = 1,4-diazabicyclo[2.2.2]octane, pzdc = pyrazine-2,3-dicarboxylate, dpyg = 1,2-di(4-pyridyl)-glycol, atz = 3-amino-1,2,4-triazolate, btc = 1,3,5-benzenetricarboxylate.

¶ Crystal data for DUT-13: $M = 1268.40 \text{ g mol}^{-1}$, trigonal, $R3c$, $a = 25.682(4)$, $c = 114.90(2) \text{ \AA}$, $V = 65\,630(18) \text{ \AA}^3$, $Z = 12$, $T = 293(2) \text{ K}$, $\rho = 0.385 \text{ g cm}^{-3}$, $\mu = 0.450 \text{ cm}^{-1}$ (solvent free), $\lambda = 0.88561 \text{ \AA}$, $1.22^\circ < \theta < 35.92^\circ$, 167 128 measured reflections, 16 481 independent, data were processed with PLATON¹⁹ Squeeze routine $R_{\text{int}} = 0.048$, R_1 (observed reflections) = 0.0542, wR_2 (all reflections) = 0.1644, max./min. residual electron density: 0.458/−0.522.

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