

# A new metal–organic framework with ultra-high surface area†

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**A new mesoporous MOF, Zn<sub>4</sub>O(bpdc)(btctb)<sub>4/3</sub> (DUT-32), containing linear ditopic (bpdc<sup>2-</sup>; 4,4'-biphenylenedicarboxylic acid) and tritopic (btctb<sup>3-</sup>; 4,4',4''-[benzene-1,3,5-triyltris(carbonylimino)]tris-benzoate) linkers, was synthesised. The highly porous solid has a total pore volume of 3.16 cm<sup>3</sup> g<sup>-1</sup> and a specific BET surface area of 6411 m<sup>2</sup> g<sup>-1</sup>, adding this compound to the top ten porous materials with the highest BET surface area.**

During the last two decades metal–organic frameworks (MOFs) have continuously set new records in terms of specific surface area and pore volume, pushing the high pressure storage capacity for energetic molecules such as hydrogen and methane further and further.<sup>1</sup>

In order to avoid the disadvantageous formation of interpenetrated structures we propose the use of two different types of elongated linkers, one with a polar functionality, and another with a purely aromatic core structure. In the following we will show that this concept leads to a highly porous non-interpenetrated MOF structure but requires a distinct activation procedure due to the stronger interaction forces between solvating molecules and the polar functional groups of one linker.

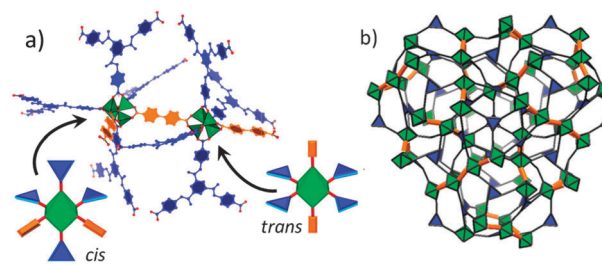
As the polar tritopic linker 4,4',4''-[benzene-1,3,5-triyltris(carbonylimino)]trisbenzoic acid (H<sub>3</sub>btctb), which has been very successfully applied in the synthesis of porous MOFs,<sup>2</sup> was used. 4,4'-Biphenylenedicarboxylic acid (H<sub>2</sub>bpdc) was chosen as the more hydrophobic linker because of the ideal di- and tritopic linker length ratio (*L<sub>D</sub>*/*L<sub>T</sub>*) of 0.63. According to Matzger *et al.*, for the formation of copolymerization MOFs, the geometric factor describing the length ratio of the linkers as well as the connectivity to the

cluster plays a key role in the formation of the given structure.<sup>3</sup> For known MOFs the *L<sub>D</sub>*/*L<sub>T</sub>* ratios lie within a region from 0.44 to 0.66 (Table S1, ESI†).

The solvothermal reaction of H<sub>3</sub>btctb and H<sub>2</sub>bpdc with zinc nitrate yields coffin-shaped transparent crystals of Zn<sub>4</sub>O(bpdc)(btctb)<sub>4/3</sub> (DUT-32, DUT – Dresden University of Technology), while an excess of H<sub>3</sub>btctb or H<sub>2</sub>bpdc in the reaction mixture leads to the formation of byproducts: Zn<sub>4</sub>O(btctb)<sub>2</sub> (DUT-59), Zn<sub>4</sub>O(btctb)<sub>2</sub>(DMF)(H<sub>2</sub>O)<sub>1.5</sub> (ref. 2a) or Zn<sub>4</sub>O(bpdc)<sub>3</sub> (IRMOF-10).<sup>4</sup> DUT-59 is isorecticular to MOF-177<sup>5</sup> (for more details see ESI†).

Interestingly, DUT-32 has a framework isorecticular to UMCM-2<sup>6</sup> with a rare **umt** topology crystallizing in the *P6<sub>3</sub>/m* space group.† The phase purity of bulk samples of DUT-32 was confirmed by powder X-ray diffraction measurements (see ESI†). The overall composition of the solvated material was determined by thermal (Fig. S7, ESI†) and elemental analysis, as well as <sup>1</sup>H-NMR (Fig. S8, ESI†), and can be described as Zn<sub>4</sub>O(bpdc)(btctb)<sub>4/3</sub>(DEF)<sub>39.7</sub>(H<sub>2</sub>O)<sub>11.3</sub>.

The structure of DUT-32 consists of two symmetry-independent Zn<sub>4</sub>O<sup>6+</sup> octahedral secondary building units. Both of them are surrounded by four btctb<sup>3-</sup> and two bpdc<sup>2-</sup> linkers. The ditopic bpdc<sup>2-</sup> ligands at the first Zn<sub>4</sub>O<sup>6+</sup> cluster are arranged in a *trans* orientation, while the *cis* orientation of linkers relative to each other is found at the second cluster (Fig. 1 and Fig. S5, ESI†). With these types of connectivity, a 3D framework is constructed with



**Fig. 1** (a) Two crystallographically independent diastereomeric SBUs in DUT-32; (b) simplified representation of DUT-32. Cluster – green, tritopic linker – blue, ditopic linker – orange.

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three different but huge mesopores ( $30 \times 40 \text{ \AA}$ ,  $28 \times 32 \text{ \AA}$  and  $20 \times 26 \text{ \AA}$ , considering van der Waals radii of the atoms), and one smaller micropore ( $14 \times 18 \text{ \AA}$ ) (Fig. S1 and S2, ESI†). The crystallographic density of the desolvated DUT-32 is extremely low, only  $0.27 \text{ g cm}^{-3}$ , and is close to the density of MOF-210 ( $0.25 \text{ g cm}^{-3}$ ).<sup>7</sup>

However, not only the crystallographic porosity, but also real gas accessible volume of the compound generated after removal of solvent molecules are crucial for the manufacture of porous materials for numerous areas of application. Activation of DEF-containing DUT-32 samples by conventional heating under vacuum results in a non-porous materials. Similar results were observed for the solvent-exchange activation method using dichloromethane, chloroform or alcohols like methanol or ethanol.

For supercritical drying, the amide solvent incorporated into the pores was exchanged first with absolute ethanol, which shows high miscibility with liquid  $\text{CO}_2$  and is commonly used for MOF activation. The resulting material exhibits an unexpected type IV nitrogen physisorption isotherm and relatively low BET surface area ( $838 \text{ m}^2 \text{ g}^{-1}$ ) and micropore volume ( $0.36 \text{ cm}^3 \text{ g}^{-1}$ ) (Fig. S9, ESI†) indicating a network distortion. However, a very high total pore volume of  $2.91 \text{ cm}^3 \text{ g}^{-1}$  was calculated. PXRD measurements performed for the sample after drying indicate a complete loss of crystallinity.

Interestingly, a resolution of this amorphous material with DEF and heating at  $373 \text{ K}$  for one day restores the crystallinity partly (Fig. S6a, ESI†). We suggest that due to its ability to form hydrogen bonds, ethanol binds quite strongly to the amide moieties of the network. Therefore, a complete exchange of the ethanol by  $\text{CO}_2$  within the pores does not occur, leading to a structural rearrangement with a loss of crystallographically defined porosity during removal of residual ethanol. A complete structural collapse of the network probably does not occur because of the extremely high total pore volume which is close to the theoretical value of  $3.21 \text{ cm}^3 \text{ g}^{-1}$ , the completely intact morphology of the dried crystals and the recovery of the network by resolution.

For the supercritical drying process the choice of the solvent is mainly based on its miscibility with liquid  $\text{CO}_2$ .<sup>8,9</sup> Therefore, the influence of solvents with minor polarity on the porosity was investigated. Applying the same drying protocol but using anhydrous acetone instead of ethanol on the same material (sample mass  $100 \text{ mg}$ ) with a resting time in  $\text{CO}_2$  of one day (replacing the liquid  $\text{CO}_2$  3 times a day) resulted in a material with completely different textural properties. PXRD measurements show that the crystallinity of the sample remains intact (Fig. S6, ESI†). This is also reflected in the  $\text{N}_2$  physisorption isotherm which shows a typical shape for a MOF material with small mesopores and reaches saturation at  $935 \text{ cm}^3 \text{ g}^{-1}$ , indicating a total pore volume of  $1.44 \text{ cm}^3 \text{ g}^{-1}$  (Fig. S9b, ESI†).

However, this value remains too low in comparison to the geometrically calculated pore volume of  $3.21 \text{ cm}^3 \text{ g}^{-1}$ , indicating insufficient activation. Interestingly, upon decreasing the amount of the sample for SCD drying from  $100 \text{ mg}$  to  $30 \text{ mg}$  and keeping the resting time in liquid  $\text{CO}_2$  and replacement cycles the same (one day, three times a day, respectively), a

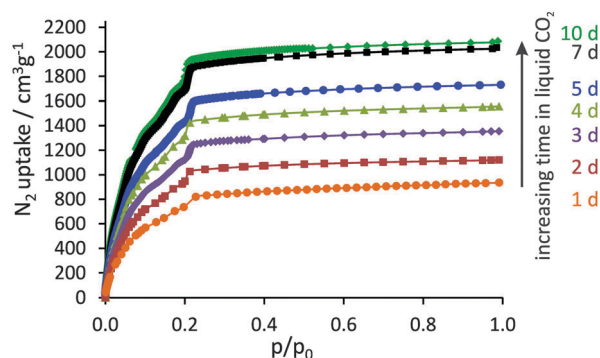


Fig. 2  $\text{N}_2$  physisorption isotherms at  $77 \text{ K}$  of DUT-32 after supercritical drying from amyl acetate as solvent with different resting times in liquid  $\text{CO}_2$  during the drying process.

sample with a significantly enhanced porosity was obtained. The adsorbed  $\text{N}_2$  volume reaches a value of  $1470 \text{ cm}^3 \text{ g}^{-1}$  representing a total pore volume of  $2.27 \text{ cm}^3 \text{ g}^{-1}$  (Fig. S9b, ESI† circles). Similar results can be observed by using amyl acetate instead of acetone indicating that for larger amounts of the sample the solvent exchange process with liquid  $\text{CO}_2$  takes more time. These results show that the MOF/liquid  $\text{CO}_2$  ratio as well as resting time in liquid  $\text{CO}_2$  (or corresponding  $\text{CO}_2$  exchange frequency) have a crucial impact on the textural properties of DUT-32.

It could be shown that by systematically extending the resting time in liquid  $\text{CO}_2$  (and exchange frequency), the porosity of DUT-32 can be significantly improved, finally reaching the theoretical limit (Fig. 2). The nitrogen uptake at  $77 \text{ K}$  increases steadily from  $935 \text{ cm}^3 \text{ g}^{-1}$  (one day in liquid  $\text{CO}_2$ ) up to a maximum of  $2040 \text{ cm}^3 \text{ g}^{-1}$  (seven days in liquid  $\text{CO}_2$ ). The maximum value corresponds to a specific pore volume of  $3.16 \text{ cm}^3 \text{ g}^{-1}$ , which is remarkable. A further increase of exchange time to ten days showed only a slight porosity improvement with an adsorbed volume of nitrogen of  $2080 \text{ cm}^3 \text{ g}^{-1}$ .

Applying consistency criteria suggested by Rouquerol and Llewellyn<sup>10</sup> to the  $\text{N}_2$  physisorption isotherm for a sample with a resting time of seven days in liquid  $\text{CO}_2$  (further denoted as DUT-32\_7d) results in an apparent BET surface area as high as  $6411 \text{ m}^2 \text{ g}^{-1}$  (see ESI†). This value is close to the geometrical surface area of DUT-32 calculated using the Poreblazer V1.2 program<sup>11</sup> ( $5981 \text{ m}^2 \text{ g}^{-1}$ ). Additionally, the nitrogen adsorption isotherm was simulated using multipurpose simulation code MUSIC.<sup>12</sup> The simulated isotherm fits well with the experimental one (Fig. S13, ESI†). By applying the BET theory to the simulated isotherm in the same relative pressure region as for the experimental one ( $p/p_0$  0.09–0.13), the surface area of  $6255 \text{ m}^2 \text{ g}^{-1}$  was calculated.

DUT-32 also has excellent gas storage properties. For  $\text{H}_2$  the excess maximum capacity is achieved at 53 bar and reaches  $85 \text{ mg g}^{-1}$  ( $7.8 \text{ wt}\%$ ;  $22.9 \text{ mg cm}^{-3}$ ) (Fig. 3) which is only surpassed by MOF-210 ( $86 \text{ mg g}^{-1}$ )<sup>7</sup> and NU-100 ( $99.5 \text{ mg g}^{-1}$ ).<sup>13</sup> Considering the enormous pore volume, the total capacity at 80 bar corresponds to  $166 \text{ mg g}^{-1}$  ( $14.21 \text{ wt}\%$ ;  $44.9 \text{ mg cm}^{-3}$ ) which is among the highest gravimetric values reported for porous materials.

Recently Yildirim *et al.*<sup>1c</sup> claimed that a hypothetical MOF with optimal methane storage properties should have a pore



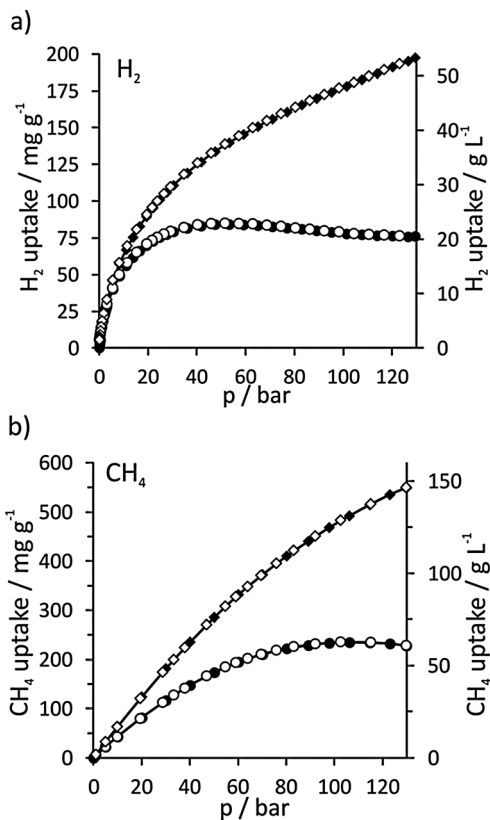


Fig. 3 H<sub>2</sub> (a, 77 K) and CH<sub>4</sub> (b, 298 K) physisorption isotherms of DUT-32\_7d; excess (●), total (◆); filled and empty symbols correspond to the adsorption and desorption, respectively.

volume of 3.2 cm<sup>3</sup> g<sup>-1</sup>, a density of 0.27 g cm<sup>-3</sup> and a surface area of 7500 m<sup>2</sup> g<sup>-1</sup> to be able to adsorb 0.5 g methane per gram of MOF (195 cc (STP) cc<sup>-1</sup>) at 65 bar. Interestingly, DUT-32 has the porosity characteristics which are very close to those of the desired hypothetical MOF: pore volume of 3.16 cm<sup>3</sup> g<sup>-1</sup> and density of 0.27 g cm<sup>-3</sup>. DUT-32's maximum excess methane capacity at 298 K is reached with 0.24 g g<sup>-1</sup> at 105 bar (corresponding to 65 mg ml<sup>-1</sup>). Due to the large pore volume, DUT-32 achieves a total desired CH<sub>4</sub> storage capacity of 0.55 g g<sup>-1</sup> (149 g L<sup>-1</sup>, 210 cm<sup>3</sup> (STP) cm<sup>-3</sup>) at 130 bar.

Summarizing, we have presented a new metal-organic framework (DUT-32) with a rare **umt** topology that can be easily scaled up due to the simple linker synthesis using cheap starting materials. Careful adjustment of the activation conditions revealed an ultrahigh porosity with a nitrogen uptake of

2080 cm<sup>3</sup> g<sup>-1</sup> (STP) corresponding to a total pore volume of 3.16 cm<sup>3</sup> g<sup>-1</sup> and an apparent BET area of 6411 m<sup>2</sup> g<sup>-1</sup>, adding this compound to the top ten materials with the highest BET surface area.

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## Notes and references

‡ Crystallographic data: C<sub>252.5</sub>H<sub>491.3</sub>N<sub>68</sub>O<sub>43.7</sub>Zn<sub>4</sub>, *M* = 5441.09 g mol<sup>-1</sup>, hexagonal, *P*6<sub>3</sub>/*m* (Nr. 176), *a* = 50.710(7) Å, *c* = 62.920(13) Å, *V* = 140 122(40) Å<sup>3</sup>, *Z* = 18, *ρ*<sub>calc.</sub> = 1.161 g cm<sup>-3</sup>, *λ* = 0.88561 Å, *T* = 293 K, *2θ*<sub>max</sub> = 28.2°, reflections collected/unique 118 656/60 048, *R*<sub>int</sub> = 0.0497, *R*<sub>1</sub> = 0.0688, *wR*<sub>2</sub> = 0.1815, *S* = 1.010, largest diff. peak 0.229 e Å<sup>-3</sup> and hole -0.196 e Å<sup>-3</sup>. CCDC 968887.

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