Porous Materials

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# A Mesoporous Metal–Organic Framework**

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A new class of porous materials namely metal–organic frameworks (MOFs) has set records in recent years regarding specific surface area and pore volume.[1–4] Nevertheless, the search for compounds with very large pores and higher specific surface area remains a key challenge in the rapidly expanding field of MOFs, especially for applications in catalysis,[5] drug delivery,[6] and high-pressure gas storage.[7–9] Compounds containing small windows or pores that are inaccessible for anchoring molecular catalysts, impregnation with catalyst precursors, or larger drug molecules pose limitations for MOFs in fine chemical transformation, nanoparticle formation, or drug delivery. For energy-storage applications at 200 bar, larger pores (2-3 nm) are essential to achieve a shift of the excess adsorption maximum towards higher pressure. Despite a somewhat reduced heat of adsorption, in practice such large pore MOFs outperform small pore MOFs as a result of the higher pore volume.

A common concept to enhance the pore size in MOFs uses a linear extension of the linker in a given network topology. In such MOFs the pore diameter achievable is limited by interpenetration. A prominent example is the IRMOF series (isoreticular MOFs).[10] Other examples of increasing pore size through linker extensions are $[Cu_3(btc)_2]$[11] (btc = benzene-1,3,5-tricarboxylate; **tbo**-topology), PCN-6[12] ($[Cu_3(tatb)_2]$, tatb = 4,4′,4″-*s*-triazine-2,4,6-triyltribenzoate; **tbo**), or MOF-14[13] ($[Cu_3(btb)_2]$, btb = benzene-1,3,5-tribenzoate; **pto**), built from paddle wheel clusters and tritopic linkers. However, in PCN-6 and MOF-14, which have the btb linker (a longer version of the btc linker), the porosity is reduced because of the presence of two interwoven 3D nets in the structure. The non-interpenetrated analogue of PCN-6 (PCN-6′)[14] is obtained using a templating strategy, while a non-interpenetrated analogue of MOF-14 is unknown.

Herein, we report an approach that avoids interpenetration by using a secondary linker to stabilize a highly open framework structure by crosslinking an extended $Pt_3O_4$-topology. The resulting new mesoporous MOF material, DUT-6 (DUT = Dresden University of Technology), shows no interpenetration and has an extremely high gas adsorption capacity for *n*-butane, hydrogen, and methane.

Single crystals of $[Zn_4O(2,6\text{-ndc})(btb)_{4/3}(def)_{16}(H_2O)_{9/2}]$ (DUT-6; def = *N*,*N*-diethylformamide, 2,6-ndc = 2,6-naphthalenedicarboxylate) suitable for X-ray diffraction analysis were obtained from the reaction of $H_3$(btb), $H_2$(2,6-ndc), and zinc nitrate in a ratio of 3:2:14. The compound crystallizes in the cubic space group $Pm\bar{3}n$. Dodecahedral mesoporous cages 2.5–3 nm in diameter are formed by twelve $Zn_4O^{6+}$ nodes, four 2,6-ndc linkers, and eight btb linkers (Figure 1 a).

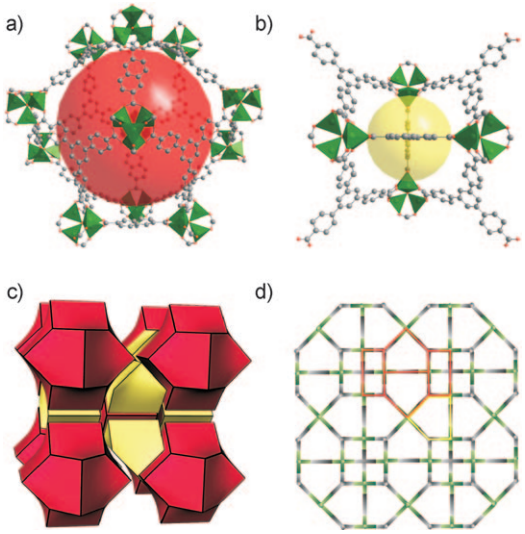


***Figure 1.*** a) Mesopore (red sphere indicates pore volume), b) small cage (yellow sphere indicates pore volume), c) topology of DUT-6; d) simplified network (clusters green, btb linkers gray; the red line shows the mesopore and the yellow line the small cage.

A second type of pore constructed from four $Zn_4O^{6+}$ clusters, two 2,6-ndc linkers, and four btb linkers is present in the structure (Figure 1 b). These smaller pores are arranged to connect the larger dodecahedral pockets to form a periodic space filling (Figure 1 c). However, void analysis using PLATON[15] indicates only one accessible mesopore type with the center at *0 0 0*. The smaller intermesopore cages are inaccessible (pore volume below 25 Å$^3$). The solvent-accessible volume in DUT-6 is 21 902 Å$^3$ equal to 79.2 % of the total cell volume. This value is consistent with the amount of

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solvent molecules determined from elemental analysis and thermogravimetric analysis (TGA). DUT-6 has a high thermal stability up to 380 °C (see Figure S3 in the Supporting Information).

The secondary building unit (SBU) consists of a $Zn_4O^{6+}$ cluster which coordinates to six bridging carboxylate groups in an octahedral arrangement. The carboxylate groups come from four btb linkers in a square planar arrangement similar to the paddle-wheels in MOF-14,[13] while two additional 2,6-ndc linkers occupy the residual octahedral sites and further crosslink the network. Thus, $Zn_4O^{6+}$ clusters and btb linkers form the four- and three-connecting nodes of a (3,4)-connected net with $Pt_3O_4$ topology further crosslinked with a secondary bifunctional 2,6-ndc linker (Figure 1 b,c).

To date only two highly porous MOFs have been synthesized using btb and a dicarboxylic acid, namely UMCM-1 ($[Zn_4O(1,4\text{-bdc})(btb)_{4/3}]$ (bdc = 1,4-benzenedicarboxylate) and UMCM-2 ($[Zn_4O(t^2dc)(btb)_{4/3}]$ ($t^2dc$ = thieno-[3,2-b]thiophene-2,5-dicarboxylate)).[3,16] However, DUT-6 has a new and completely different network topology. The compound has a rigid framework and exhibits high permanent porosity, which has been confirmed by gas- and liquid-phase adsorption, and by the adsorption of large molecules.

The nitrogen adsorption isotherm of DUT-6 at −196 °C (Figure 2 a) reaches saturation at 1380 $cm^3 g^{-1}$. The total pore volume is 2.02 $cm^3 g^{-1}$. These values are among the highest values reported for MOFs (MOF-5: $N_2$ saturation uptake (SU) 830 $cm^3 g^{-1}$, pore volume ($V_P$) 1.05 $cm^3 g^{-1}$,[10] MOF-177 (SU: 1350 $cm^3 g^{-1}$, $V_P$: 1.59 $cm^3 g^{-1}$),[1] MIL-101 (SU: 1200 $cm^3 g^{-1}$, $V_P$: 1.5–1.9 $cm^3 g^{-1}$),[2] UMCM-2 (SU: 1500 $cm^3 g^{-1}$)[3]).

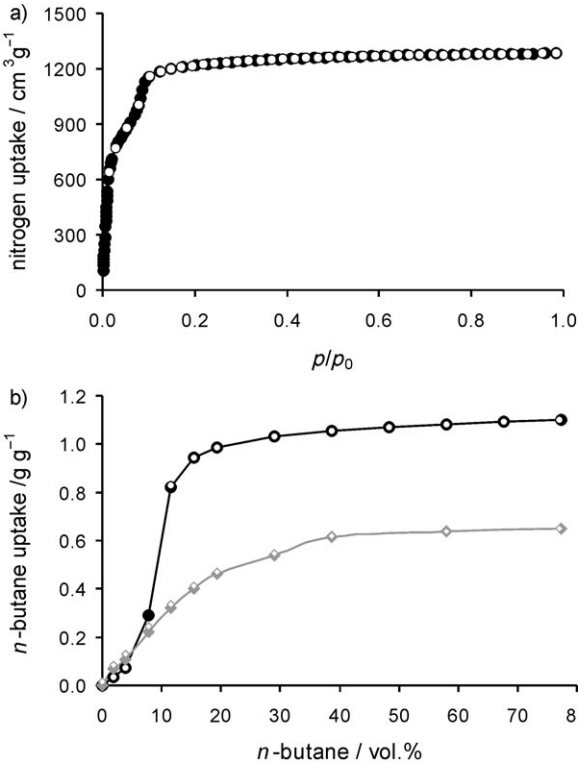


***Figure 2.*** a) Nitrogen (−196 °C) adsorption (●) and desorption (○) isotherms of DUT-6; b) *n*-butane (20 °C) adsorption (●/◆) and desorption (○/◇) of DUT-6 (black) and MIL-101 (gray).

The volumetric hydrogen adsorption isotherm for DUT-6 (Figure 3 a) revealed an excess hydrogen-storage capacity of 666 $cm^3 g^{-1}$ at 50 bar corresponding to 60 $mg g^{-1}$ (5.64 wt %), which is one of the highest values reported to date for hydrogen adsorption by MOFs.[9]

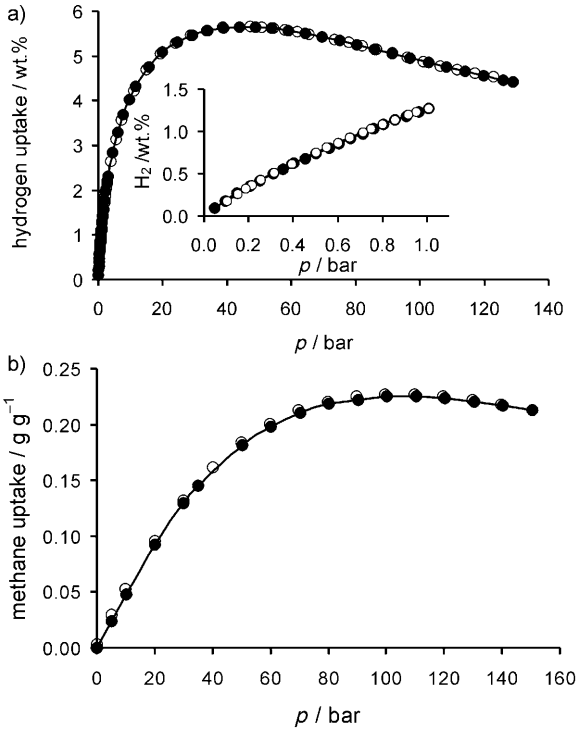


***Figure 3.*** High-pressure excess adsorption (●) and desorption (○) isotherms of DUT-6 for a) hydrogen (−196 °C) inset: low-pressure region and b) methane (25 °C).

The methane physisorption isotherm was measured using a magnetic suspension balance up to 150 bar at 25 °C. At 35 bar DUT-6 has an excess uptake of 145 $mg g^{-1}$ (79 $cm^3 cm^{-3}$ based on the crystallographic density). The saturation in the adsorption occurs at higher pressure because of the mesoporous character of DUT-6 and the maximum amount adsorbed is 230 $mg g^{-1}$ (126 $cm^3 cm^{-3}$) at 100 bar. DUT-6 thus has one of the highest gravimetric methane-adsorption capacities in the high pressure region reported for MOFs.[8,10,18]

An important model substance for the removal of hydrophobic solvent molecules and toxic compounds from air is *n*-butane. The measurement with
*n*-butane was carried out at 20 °C under atmospheric pressure and dynamic conditions
(*n*-butane diluted with nitrogen). DUT-6 stores up to 1.1 $g g^{-1}$ *n*-butane. This is five-times more than observed for the commercially available MOF $[Cu_3(btc)_2]$ and even surpasses the *n*-butane adsorption capacity of the mesoporous MIL-101 (Figure 2 b).[17]

Liquid-phase adsorption experiments were used to demonstrate the access of large molecules to the mesopores inside

  

DUT-6. Reichardt's dye and $C_{60}$ are adsorbed resulting in the initially transparent DUT-6 crystals becoming colored. The size-selective adsorption of $C_{60}$ versus [6,6]-phenyl-$C_{61}$-butyric acid methyl ester confirms the uniformity of the pore system (Figure S2 in the Supporting Information).

The liquid-phase adsorption of ethylcinnamate in *n*-heptane at 25 °C again demonstrates the extremely high adsorption capacity of DUT-6 (Figure 4). In this experiment

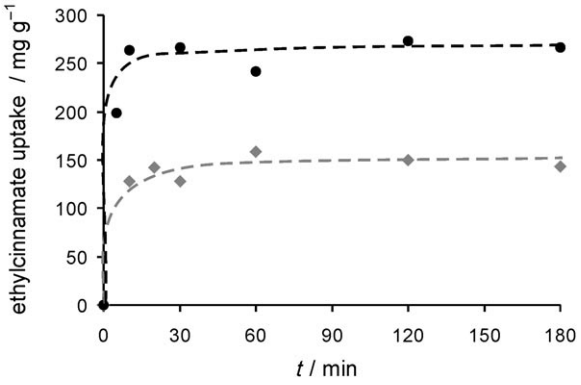


***Figure 4.*** Liquid-phase adsorption of ethylcinnamate in DUT-6 (●) and MOF-5 (◆) at 25 °C.

DUT-6 shows an adsorption capacity that is twice as high as that of MOF-5[19] at the same adsorption rate. X-ray diffraction patterns before and after the experiment are identical, demonstrating the stability of the network during the adsorption experiment.

Summarizing, a novel metal–organic framework with uniform mesopores $[Zn_4O(2,6\text{-ndc})(btb)_{4/3}(def)_{16}(H_2O)_{9/2}]$ (DUT-6) was obtained. Secondary crosslinking of a $Pt_3O_4$ topology allows interpenetration to be avoided resulting in extremely high permanent porosity. The wide open pores lead to enormously high methane (230 mg g$^{-1}$) and hydrogen (60 mg g$^{-1}$; 5.64 wt %) uptake and the highest *n*-butane adsorption capacity reported for MOFs (1.1 g g$^{-1}$).

## Experimental Section

General Information: Commercially available reagents were used as received. The DEF used for the MOF synthesis was dried over $P_2O_5$. The elemental analysis for C, H, and N were performed with CHNS 932 analyzer (LECO) and for O in combination with a VTF-900 oven. The analysis of Zn was carried out with ICP-OES Vista RL (Varian).

DUT-6: $Zn(NO_3)_2{\cdot}4H_2O$ (0.142 g, 0.543 mmol), $H_2$(2,6-ndc) (0.017 g, 0.079 mmol), and $H_3$(btb) (0.054 g, 0.123 mmol) were dissolved in DEF (10 cm$^3$). The mixture was sonicated for 5 min and heated to 100 °C for 24 h in a Pyrex tube. After cooling to room temperature the product was isolated by decanting the mother liquid and washed with DEF. Yield: 49 %. The resulting solid was immersed in $CH_2Cl_2$ for 2 days. During this time the $CH_2Cl_2$ was replaced with fresh $CH_2Cl_2$ three times. Elemental analysis calcd (%) for $C_{128}H_{211}O_{33.5}N_{16}Zn_4$: C 55.5, H 7.67, O 19.34, N 8.09, Zn 9.44; found: C 56.2 ± 0.3, H 7.66 ± 0.07, O 19.95 ± 0.09, N 8.01 ± 0.08, Zn 9.22 ± 0.05. The phase purity of the product was also confirmed by X-ray powder diffraction analysis (Figure S1 in the Supporting Information).

Adsorption experiments: $N_2$ and low-pressure $H_2$ physisorption isotherms were measured up to 1 bar using a Quantachrome Autosorb1C apparatus. High-pressure $H_2$ adsorption measurement at −196 °C up to 135 bar was performed using approximately 0.7 g sample on a volumetric BELSORP-HP apparatus. High-pressure $CH_4$ adsorption was studied using a magnetic suspension balance (Rubotherm). Adsorption of *n*-butane was performed with a microbalance (B111, Setaram) at ambient conditions. High-purity gases were used ($N_2$: 99.999 %, $H_2$: 99.999 %, $CH_4$: 99.5 %, *n*-$C_4H_{10}$: 99.95 %). The liquid-phase adsorption was performed using a 0.1 mol L$^{-1}$ solution of ethylcinnamate in *n*-heptane at 25 °C. The activated sample was added to the solution and stirred for 3 h. The adsorption process was monitored by GC-MS analysis (SHIMADZU GCMS QP5000 with a BPX5 SGE column). Prior to all adsorption measurements, the samples were evacuated for 16 h at 30 °C.

Crystal-structure determination: The crystal of DUT-6 was sealed in a glass capillary with a small amount of DEF. 100 frames were collected (scan width 1°; exposure time 1.2 s/frame (0.29 mm aluminum filter)) at 20 °C using synchrotron radiation on beamline BL14.2 of the Joint Berlin-MX Laboratory at BESSY-II (Berlin, Germany) with a MX-225 CCD detector (Rayonics, Illinois). The data were integrated and scaled with the XDS software package.[20] The structure was solved using direct methods with the help of SHELXS-97[21] and refined by full-matrix least-squares techniques using SHELXL-97.[22] As in IRMOF-8[10] the 2,6-ndc is disordered (Figure S4 in the Supporting Information). Owing to the high symmetry of the space groups and low residual electron density it was impossible to locate DEF and $H_2O$ guest molecules. Non-hydrogen atoms were refined with anisotropic temperature parameters. The hydrogen atoms were positioned geometrically and refined using a riding model. Crystal data: $C_{48}H_{26}O_{13}Zn_4$, $M_r = 1072.16$, cubic, $Pm\bar{3}n$ (Nr. 224), $a = 30.245(4)$ Å, $V = 27667(6)$ Å$^3$, $Z = 6$, $\rho_{calcd} = 0.386$ g cm$^{-3}$, $\lambda = 0.88561$ Å, $T = 20$ °C, $2\theta_{max} = 57.6°$, reflections collected/unique 71990/3339, $R_{int} = 0.0613$, $R_1 = 0.0982$, $wR_2 = 0.2864$, largest diff. peak 0.776 e Å$^{-3}$ and hole −0.393 e Å$^{-3}$. CCDC 741720 contains 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. The topology of the network was analyzed with the program package TOPOS.[23]

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