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Assembly of metal–organic polyhedra into highly porous frameworks for ethene delivery†

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Two new mesoporous metal–organic frameworks (DUT-75 and DUT-76) with exceptional ethene uptake were obtained using carbazole dicarboxylate based metal–organic polyhedra as supermolecular building blocks. The compounds have a total pore volume of 1.84 and 3.25 cm³ g^{−1} and a specific BET surface area of 4081 and 6344 m² g^{−1}, respectively, and high gas uptake at room temperature and high pressure.

Small gas molecules such as NO¹ or ethene² act as important stimuli in biological systems. Ethene is a phytohormone that is involved in a number of plant stress responses and developmental processes, including ripening.³ The involvement of such molecules in many biological processes has fueled interest in the storage and delivery of gaseous bio relevant molecules and a variety of systems (nanoparticle, porous materials, molecular complexes) were discussed for NO or ethene storage and delivery.⁴ Recently, metal–organic frameworks (MOFs) as a new class of highly porous materials were proposed for the storage and release of NO.⁵ Especially the presence of accessible metal sites in MOFs is beneficial due to affinity enhancement associated with specific coordination modes of the substrate. While NO storage was addressed to a wide extent, the adsorption of ethene is still a scarcely investigated field of research.⁶ The latter is astonishing, considering the importance in chemical industry for polymerization reactions, tremendous potential in separation applications and the widespread use of ethene in ripening applications of fruits. In this context, there is considerable need to develop novel materials with high ethene storage capacity.

An ideal tool to achieve porous compounds with desired topology and porosity is to use metal–organic polyhedra (MOPs),

such as MOP-1, as building blocks.⁷ The process of creating 3D porous structures through controlled assembly of these polyhedra by well-defined junctions provides us with a maximum of control over the resulting structure and topology. Recently, the potential of MOP assembly using a carbazole based MOP for the design of MOFs with ultrahigh porosity was demonstrated by Kaskel⁸ and Zhou.⁹ The cuboctahedral 12-connecting MOP is an ideal building block for the design of highly porous MOFs containing a high number of open metal sites. DUT-49, an interconnected **fcu** network of MOPs contains 2.5 mmol Cu per gram of framework and represents the world record in terms of gravimetric methane excess adsorption capacity (DUT – Dresden University of Technology).¹⁰ However, the connection of cuboctahedral 12 connecting MOPs (Fig. 1a) *via* the carbazole nitrogen as the connecting point as presented in DUT-49 does not increase the number of accessible metal sites but mostly enhances the pore volume. In order to assemble highly porous structures while increasing the density of open metal sites for ethene adsorption, we designed two new isorecticular tritopic ligands H₃CPCDC (9-(4-carboxyphenyl)-9H-carbazole-3,6-dicarboxylic acid) and H₃CBCDC (9-(4'-carboxy-[1,1'-biphenyl]-4-yl)-9H-carbazole-3,6-dicarboxylic acid) (Fig. 1d, for synthetic details see ESI†) to achieve a (4,12)-connected net with **ftw** topology, in which additional paddle-wheels with accessible and open metal sites serve as connectors.

Solvothermal reaction of these ligands (L) with Cu(NO₃)₂·3H₂O in a mixture of *N,N*-dimethylformamide (DMF) and EtOH afforded DUT-75 and DUT-76 with overall chemical composition Cu₃(L)₂(H₂O)_x(DMF)_y(EtOH)_z.

Single crystal X-ray diffraction analysis reveals that both, DUT-75 and DUT-76, are isorecticular to each other and crystallize in the cubic space group *Pm* $\bar{3}$ *m*. $\ddagger$ Topological analysis of the structure indicates a (3,4,4)-connected net, if all paddle-wheels are considered as square nodes (Fig. 1d). This rare network is not described in the RCSR-database¹¹ so far and thus represents a new framework topology. The structures contain two different symmetrically independent copper paddle-wheels. The first is involved in formation of the carbazole based MOPs. The second paddle-wheel is responsible for MOP connection. In general, the structure of

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† Electronic supplementary information (ESI) available: Synthetic procedures for H₃CPCDC, H₃CBCDC, DUT-75 and DUT-76; details of crystal structure determination; X-ray powder diffraction data, physisorption and thermogravimetric data. CCDC 982441 and 982442. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc07920e

Fig. 1 (a) Carbazole based metal–organic polyhedron (left) as cuboctahedral 12-connecting SBB (right); (b) four linker molecules connected by a copper paddle-wheel SBU in DUT-75; (c) crystal structure of DUT-75 with three different cavities: cuboctahedral (yellow), tetragonal (blue), cubic (green); (d) topological representation of the (3,4,4)-connected net of DUT-75 and DUT-76; (e) representation of an augmented **ftw** net; (f) tiling of DUT-75 and -76: cuboctahedral cavity (red), tetragonal cavity (blue), cubic cavity (green).

Table 1 Pore sizes of DUT-75 and DUT-76 in Ångström

Pore type/Wyckoff position	DUT-75	DUT-76
Cuboctahedral/1b	12	12
Tetragonal/3c	4.5 × 18	11 × 21
Cubic/1a	21	27

DUT-75 and -76 can be understood as 12-connecting cuboctahedral supermolecular building blocks (SBBs) connected by square-planar 4-connecting secondary building units (SBUs) (Fig. 1b) resulting in a (4,12)-connected net with an augmented **ftw** topology (Fig. 1e).

The DUT-75 and -76 frameworks contain tetragonal and cubic cavities in addition to the MOP voids (Fig. 1f). Thus DUT-75 and -76 have a trimodal pore structure (Table 1). The limiting diameter of the MOP window is 5.8 Å. The tetragonal and cubic cavities are interconnected by large windows to give an extended 3D pore structure. The total solvent accessible volume of the desolvated frameworks (after removal of all guests and coordinated solvent molecules) was determined using PLATON to be 80.4% for DUT-75 and 86.0% for DUT-76, rendering especially DUT-76 one of the most porous MOF materials synthesized to date. Moreover, the concentration of open metal sites in the new compound could be increased to 3.2 and 2.8 mmol Cu per g in DUT-75 and DUT-76 which is a crucial requirement for enhanced gas storage of weakly coordinating molecules.

The nitrogen physisorption isotherm of DUT-75 (Fig. 2) reaches a plateau at around $p/p_0 = 0.1$, the saturation uptake is $1192 \text{ cm}^3 \text{ g}^{-1}$ and the corresponding specific pore volume (V_p) is $1.84 \text{ cm}^3 \text{ g}^{-1}$. Analysis of the adsorption data using BET theory leads to an apparent specific BET surface area (SSA) of $4081 \text{ m}^2 \text{ g}^{-1}$. Thus DUT-75 ranks among ultrahighly porous

Fig. 2 Nitrogen physisorption isotherms at 77 K of DUT-75 (circles) and DUT-76 (diamonds); adsorption – open symbols, desorption – filled symbols.

MOFs such as MOF-177 ($\text{SSA} = 4500 \text{ m}^2 \text{ g}^{-1}$, $V_p = 1.89 \text{ cm}^3 \text{ g}^{-1}$)¹² and MIL-101c ($\text{SSA} = 4230 \text{ m}^2 \text{ g}^{-1}$, $V_p = 1.9 \text{ cm}^3 \text{ g}^{-1}$).¹³

The isotherm of DUT-76 (Fig. 2) exhibits two distinct steps before reaching the plateau at $p/p_0 = 0.25$. The nitrogen uptake of DUT-76 reaches saturation at $2103 \text{ cm}^3 \text{ g}^{-1}$, corresponding to a specific pore volume of $3.25 \text{ cm}^3 \text{ g}^{-1}$. This value substantially exceeds the pore volume of most known MOFs, is close to DUT-32 ($3.16 \text{ cm}^3 \text{ g}^{-1}$),¹⁴ MOF-200 and MOF-210, ($3.59 \text{ cm}^3 \text{ g}^{-1}$ and $3.6 \text{ cm}^3 \text{ g}^{-1}$),¹² and is significantly surpassed only by the recently discovered NU-109 ($3.75 \text{ cm}^3 \text{ g}^{-1}$) and NU-110 ($4.40 \text{ cm}^3 \text{ g}^{-1}$).¹⁵ Careful analysis of the nitrogen physisorption data using the BET theory considering all consistency criteria proposed by Rouquerol and Llewellyn¹⁶ leads to an apparent specific surface area of $6344 \text{ m}^2 \text{ g}^{-1}$. This value is one of the largest specific surface areas reported so far among all porous solids. DUT-76 is one of the very few ultrahighly porous materials with a SSA above $6000 \text{ m}^2 \text{ g}^{-1}$ (MOF-210: $6240 \text{ m}^2 \text{ g}^{-1}$;¹² DUT-32: $6411 \text{ m}^2 \text{ g}^{-1}$;¹⁴ NU-110: $7140 \text{ m}^2 \text{ g}^{-1}$ (ref. 15)).

Fig. 3 Excess (circles) and total (squares) ethene adsorption isotherms of DUT-75 at 298 K; excess (diamonds) and total (triangles) ethene adsorption isotherms of DUT-76 at 298 K.

Ethene is the lightest olefin and the largest volume organic chemical, stored in large quantities in petrochemical industry for the production of polymers and other organic chemicals. Transport as a fluid is a high risk scenario due to the high reactivity and affinity for autodecomposition and polymerization rendering adsorptive storage technologies as highly attractive solutions for save delivery sources.¹⁷ Ethene uptake of DUT-75 and DUT-76 was investigated up to 70 bar at 298 K.

The high concentration of coordinatively unsaturated metal sites in DUT-75 and DUT-76 is responsible for the high storage performance, due to the selective interaction with the double bond.¹⁸ In fact, the investigated MOFs can adsorb a huge amount of ethene at room temperature (Fig. 3): the maximum excess uptake is 21.5 mmol g⁻¹ for DUT-75 at 40 bar and 30 mmol g⁻¹ for DUT-76 at 45 bar. These values are the highest ever reported in the literature.

Beyond these enormous capacities for ethene, the novel MOFs are also excellent materials for hydrogen (Fig. S9, ESI[†]), carbon dioxide (Fig. S10 and S11, ESI[†]), and methane (Fig. S12, ESI[†]) storage. The excess hydrogen adsorption of DUT-76 at 77 K reaches a maximum value of 83 mg g⁻¹ at 60 bar (total: 183 mg g⁻¹; 100 bar) which is one of the highest excess storage capacities for hydrogen reported so far (DUT-49: 80 mg g⁻¹ (excess), 165 mg g⁻¹ (total)),⁸ MOF-210: 86 mg g⁻¹ (excess), 167 mg g⁻¹ (total)).¹² Only NU-100 shows substantially higher maximum excess hydrogen uptake (99 mg g⁻¹).¹⁹ In terms of total uptake at 100 bar DUT-76 (total: 183 mg g⁻¹) surpasses even NU-100 (total: 164 mg g⁻¹).

The excellent methane storage capacity of DUT-75 (maximum excess 240 mg g⁻¹ at 90 bar and 298 K) and DUT-76 (290 mg g⁻¹ at 110 bar and 298 K) exceeds the capacities of nearly all high-performance-materials in this field²⁰ and is only surpassed by DUT-49 (308 mg g⁻¹) so far.⁸ Due to the enormous specific pore volume DUT-76 has a gigantic gravimetric uptake of 633 mg g⁻¹ at a pressure of 140 bar (commercial tank systems operate even higher at 200 bar) translating into a specific volumetric storage capacity of 243 cm³ cm⁻³. This value matches already the density of compressed natural gas at 200 bar

(239 cm³ cm⁻³) and is a promising technological milestone especially for North American markets, where shale gas exploration currently leads to a boom of natural gas driven cars and trucks. At 65 bar, the total methane uptake is 410 mg g⁻¹, which is the highest value reported in the literature and is only slightly lower than the DOE target of 500 mg g⁻¹.

In summary, the assembly of cuboctahedral building blocks into ultrahighly porous frameworks with specific surface areas up to 6344 m² g⁻¹ is a successful strategy for the realization of wide open pores and a high density of open metal sites in parallel. The latter is not only crucial to achieve high gas storage performance for energy carriers in DUT-76 but moreover an ideal concept to safely store ethene, an important phytohormone and high-volume chemical intermediate that will experience increased growth in the future.

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Notes and references

‡ Crystallographic data: DUT-75: C₄₂H₂₀Cu₃N₂O₁₅, *M* = 983.22 g mol⁻¹, cubic, *Pm*3*m*, *a* = 27.860(3) Å, *V* = 21624(4) Å³, *Z* = 6, ρ_{calc} = 0.453 g cm⁻³, λ = 0.88561 Å, *T* = 293 K, reflections collected/unique 8156/4428, *R*₁ = 0.0555, *wR*₂ = 0.1817, *S* = 0.911, largest diff. peak 0.272 e Å⁻³ and hole -0.502 e Å⁻³; DUT-76: C₅₄H₂₈Cu₃N₂O₁₅, *M* = 1135.40 g mol⁻¹, cubic, *Pm*3*m*, *a* = 33.970(4) Å, *V* = 39200(8) Å³, *Z* = 6, ρ_{calc} = 0.289 g cm⁻³, λ = 0.88561 Å, *T* = 293 K, reflections collected/unique 13443/7208, *R*₁ = 0.0453, *wR*₂ = 0.1572, *S* = 1.060, largest diff. peak 0.309 e Å⁻³ and hole -0.329 e Å⁻³. CCDC 982441 and 982442.

- 1 M. R. Miller and I. L. Megson, *Br. J. Pharmacol.*, 2007, **151**, 305.
- 2 N. Keller, M.-N. Ducamp, D. Robert and V. Keller, *Chem. Rev.*, 2013, **113**, 5029.
- 3 (a) A. B. Bleecker and H. Kende, *Annu. Rev. Cell Dev. Biol.*, 2000, **16**, 1; (b) S. P. Burg and E. A. Burg, *Science*, 1965, **148**, 1190.
- 4 (a) A. Seabra, M. Rai and N. Durán, *J. Plant Biochem. Biotechnol.*, 2014, **23**, 1; (b) S. Sortino, *Chem. Soc. Rev.*, 2010, **39**, 2903.
- 5 (a) S. Keskin and S. Kizilel, *Ind. Eng. Chem. Res.*, 2011, **50**, 1799; (b) B. Xiao, P. S. Wheatley, X. B. Zhao, A. J. Fletcher, S. Fox, A. G. Rossi, I. L. Megson, S. Bordiga, L. Regli, K. M. Thomas and R. E. Morris, *J. Am. Chem. Soc.*, 2007, **129**, 1203; (c) A. C. McKinlay, J. F. Eubank, S. Wuttke, B. Xiao, P. S. Wheatley, P. Bazin, J. C. Lavalley, M. Daturi, A. Vimont, G. De Weireld, P. Horcajada, C. Serre and R. E. Morris, *Chem. Mater.*, 2013, **25**, 1592; (d) S. R. Miller, E. Alvarez, L. Fradcourt, T. Devic, S. Wuttke, P. S. Wheatley, N. Steunou, C. Bonhomme, C. Gervais, D. Laurencin, R. E. Morris, A. Vimont, M. Daturi, P. Horcajada and C. Serre, *Chem. Commun.*, 2013, **49**, 7773.
- 6 A. Czaja, E. Leung, N. Trukhan and U. Müller, in *Metal-Organic Frameworks: Applications from Catalysis to Gas Storage*, ed. D. Farruseng, Wiley-VCH, Weinheim, 2011, pp. 339–352.
- 7 (a) J. J. Perry, J. A. Perman and M. J. Zaworotko, *Chem. Soc. Rev.*, 2009, **38**, 1400; (b) J.-R. Li and H.-C. Zhou, *Nat. Chem.*, 2010, **2**, 893; (c) V. Guillermin, D. Kim, J. F. Eubank, R. Luebke, X. Liu, K. Adil, M. S. Lah and M. Eddaoudi, *Chem. Soc. Rev.*, 2014, **43**, 6141.
- 8 U. Stoeck, S. Krause, V. Bon, I. Senkovska and S. Kaskel, *Chem. Commun.*, 2012, **48**, 10841.
- 9 W. Lu, D. Yuan, T. A. Makal, Z. Wei, J.-R. Li and H.-C. Zhou, *Dalton Trans.*, 2013, **42**, 1708.
- 10 U. Stoeck, G. Nickerl, U. Burkhardt, I. Senkovska and S. Kaskel, *J. Am. Chem. Soc.*, 2012, **134**, 17335.
- 11 M. O'Keeffe, M. A. Peskov, S. J. Ramsden and O. M. Yaghi, *Acc. Chem. Res.*, 2008, **41**, 1782.
- 12 H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. Ö. Yazaydin, R. Q. Snurr, M. O'Keeffe, J. Kim and O. M. Yaghi, *Science*, 2010, **329**, 424.
- 13 G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble and I. Margiolaki, *Science*, 2005, **309**, 2040.

- 14 R. Gröninger, V. Bon, P. Müller, U. Stöck, S. Krause, U. Müller, I. Senkowska and S. Kaskel, *Chem. Commun.*, 2014, **50**, 3450.
- 15 O. K. Farha, I. Eryazici, N. C. Jeong, B. G. Hauser, C. E. Wilmer, A. A. Sarjeant, R. Q. Snurr, S. T. Nguyen and A. Ö. Yazaydin, *J. Am. Chem. Soc.*, 2012, **134**, 15016.
- 16 J. Rouquerol, P. Llewellyn and F. Rouquerol, in *Studies in Surface Science and Catalysis*, ed. P. Llewellyn, F. Rodriguez-Reinoso, J. Rouquerol and N. Seaton, Elsevier, 2007, vol. 160, pp. 49–56.
- 17 http://atmi.com/semiconductor/solution_sds.htm.
- 18 E. D. Bloch, W. L. Queen, R. Krishna, J. M. Zadrozny, C. M. Brown and J. R. Long, *Science*, 2012, **335**, 1606.
- 19 O. K. Farha, A. Özgür Yazaydin, I. Eryazici, C. D. Malliakas, B. G. Hauser, M. G. Kanatzidis, S. T. Nguyen, R. Q. Snurr and J. T. Hupp, *Nat. Chem.*, 2010, **2**, 944.
- 20 F. Gándara, H. Furukawa, S. Lee and O. M. Yaghi, *J. Am. Chem. Soc.*, 2014, **136**, 5271.