**Dieses Dokument ist eine Zweitveröffentlichung (Verlagsversion) /
This is a self-archiving document (published version):**

Irena Senkowska, Stefan Kaskel

Ultrahigh porosity in mesoporous MOFs: promises and limitations

Erstveröffentlichung in / First published in:

Chemical Communications. 2014, 50(54), S. 7089-7098 [Zugriff am: 01.11.2019]. Royal Society of Chemistry. ISSN 1364-548X.

DOI: <https://doi.org/10.1039/c4cc00524d>

Diese Version ist verfügbar / This version is available on:

<https://nbn-resolving.org/urn:nbn:de:bsz:14-qucosa2-359577>

„Dieser Beitrag ist mit Zustimmung des Rechteinhabers aufgrund einer (DFGgeförderten) Allianz- bzw. Nationallizenz frei zugänglich.“

This publication is openly accessible with the permission of the copyright owner. The permission is granted within a nationwide license, supported by the German Research Foundation (abbr. in German DFG).

www.nationallizenzen.de/

Ultrahigh porosity in mesoporous MOFs: promises and limitations

Cite this: *Chem. Commun.*, 2014, 50, 7089

Irena Senkovska and Stefan Kaskel*

Mesoporous MOFs are currently record holders in terms of the specific surface area with values exceeding $7000 \text{ m}^2 \text{ g}^{-1}$, a textural feature unattained by traditional porous solids such as zeolites, carbons and even by graphene. They are promising candidates for high pressure gas storage and also for conversion or separation of larger molecules, whose size exceeds the pore size of zeolites. The rational strategies for synthesis of mesoporous MOF are outlined and the unambiguous consistent assessment of the surface area of such ultrahighly porous materials, as well as present challenges in the exciting research field, of mesoporous MOFs are discussed. The crystallinity, dynamic properties, functional groups, and wide range tunability render these materials as exceptional solids, but for the implementation in functional devices and even in industrial processes several aspects and effective characteristics (such as volumetric storage capacities, recyclability, mechanical and chemical stability, activation) should be addressed.

Received 21st January 2014,
Accepted 26th March 2014

DOI: 10.1039/c4cc00524d

www.rsc.org/chemcomm

The modularity of metal–organic frameworks (MOFs) or porous coordination polymers (PCPs) is manifested not only in the variety of inorganic and organic building blocks which can be used for the synthesis, and in topological connection of these to each other. It is also possible to design materials with desired pore size distributions and textural properties almost without limitations. This class of materials has a unique potential to combine the pores ranging from ultramicro up to meso pore size regime, but they can be also purely microporous or mesoporous. Even though, most of the MOFs reported to date are microporous materials, the number of reports on the mesoporous compounds with extremely high specific surface area above $4500 \text{ m}^2 \text{ g}^{-1}$ is increasing from year to year.

The International Union of Pure and Applied Chemistry (IUPAC) proposed to classify the porous materials according to the internal pore width. Microporous materials contain pores with an internal width less than 2 nm, and mesoporous materials have pores with an internal width between 2 and 50 nm. It should be mentioned that such definition rather refers to the physisorption process in porous materials and it is based on the effect of confined pore space on the adsorptive. It is reflected in the shape or type of the adsorption isotherm. In the present discussion we will deal with the crystallographically defined pore width and not strictly follow the definition based on adsorption measurements. Extrinsic porosity (for example porosity caused by the crystal defects or produced by structuralizing the crystals) will not be discussed in this article. The scientific interest

towards the mesoporous MOFs from one side is driven by the wish to test the limits of the modular concept and surface area ceiling.^{1,2} Another driving force for development of mesoMOFs is the requirements from certain application fields, such as high pressure gas storage, immobilization of large organic molecules, or biomedical catalysis.

Theoretical calculations show, for example, that the methane storage capacity at 35 bar is maximal for dominant pore diameters in the range 4–9 Å and the optimum pore diameter at 100 bar is $\sim 8 \text{ Å}$. However, MOFs with larger pores (in the range 16–20 Å) also show promising storage capacities (*i.e.*, $>200 \text{ vol (STP) vol}^{-1}$) at high pressure.³

Constitutional isomer separation as well as stereoisomer separation need new materials with high performance. To reach an acceptable separation in continuous flow, the size of the analyte molecule should be significantly smaller than the pore diameter of the porous material to avoid diffusion limitations.⁴ In the ideal case, the analyte diameter should be in between 5 and 15% of the pore diameter, which makes the presence of mesopores essential.

In the present overview, design, synthesis, activation and porosity determination, as well as functionality of mesoporous MOFs with ultra-high porosity will be discussed.

1. Synthetic strategies

1.1 Direct synthesis

IRMOF concept. The most successful strategy to extend the pores up to the mesoporous range is the systematic enlargement of the linker in the fixed framework topology.⁵ Since the

Technische Universität Dresden, Department of Inorganic Chemistry, Bergstr. 66, Dresden, Germany. E-mail: Stefan.Kaskel@chemie.tu-dresden.de; Fax: +49 0351 463 37287; Tel: +49 0351 463 34885

concept itself and first mesoporous MOF (IRMOF-16) were introduced by Yaghi *et al.* in 2002,⁶ many examples of isorecticular series successfully synthesized using this strategy were published. Also the two main problems, interpenetration⁷ and polymorphism, which often appear with increased linker length, were recognized at the early stage of MOF chemistry.^{8–10} HKUST-1 ($\text{Cu}_3(\text{btc})_2$, btc – benzene-1,3,5-tricarboxylate)¹¹ (**tbo**) and MOF-14¹² ($\text{Cu}_3(\text{btb})_2$, btb – benzene-1,3,5-tribenzoate) (**pto**) can be named as prominent examples, both built from paddle wheel clusters and tritopic linkers. First of all, these two compounds crystallize in topologically different structures: HKUST-1 in **tbo** and MOF-14 in **pto**. Additionally, MOF-14 has reduced porosity due to the presence of two interwoven 3D nets in the structure. It took 10 years after the discovery of MOF-14, to find a way avoiding the interpenetration. $\text{Cu}_3(\text{btb})_2$ (DUT-34), a non-interpenetrated counterpart (so called *framework-catenation isomer*)¹³ to MOF-14, could be obtained by adjusting the synthetic conditions only. The screening of a large number of alternative synthetic routes was needed in order to evaluate the phase purity region (Fig. 1).

Zhou and co-workers synthesized an interpenetrated MOF isorecticular to $\text{Cu}_3(\text{btc})_2$ (**tbo** topology) named PCN-6 (PCN stands for porous coordination network), as well as the non-interpenetrated counterpart of it. Addition of oxalic acid to the reaction mixture leads to a single net MOF PCN-6'.¹⁴ Another way to avoid interpenetration and to stabilize the structure, which could be realized in $\text{Cu}_3(\text{btb})_2$ (**pto**), is the overcoming of energetic stabilization provided by interpenetration by inserting a linear neutral ligand (in this case bipyridine (bipy)) between the neighboring paddle-wheels. The resulting $[\text{Cu}_2(\text{bipy})]_3(\text{btb})_4$ (DUT-23) possess high porosity after activation (pore volume up to $2.03 \text{ cm}^3 \text{ g}^{-1}$) as well as excellent performance in the adsorption of gases like methane, hydrogen and *n*-butane, which is not the case for DUT-34.¹⁵

In general, the interpenetration can be avoided through the (i) reaction temperature and concentration control; (ii) template-directed control, and (iii) ligand design/modification-induced control.⁷ As an example for (iii), in the Cu–btb system, the non-interpenetrated compound crystallizing in **tbo** topology

(counterpart to DUT-33)¹⁵ could be obtained using a substituted btb linker.¹⁶

In general, the topological structures where the interpenetration is not possible would be the more promising target systems for applying the isorecticular synthesis strategy. This was recently demonstrated by Yaghi *et al.* for the MOF-74¹⁷ (CPO-27¹⁸) structure, with the composition $\text{M}_2(2,5\text{-DOT})$ (where M is Zn^{2+} , Mg^{2+} and DOT is dioxidoterephthalate). The structure consists of infinite rod-shaped metal carboxylate SBUs linked by the linear ligand. The ligands form the walls of the channels running along one crystallographic direction. The intrinsic packing arrangement of the linkers inside the wall does not favor interpenetration. So, it was possible starting from the original DOT linker of one phenylene ring to go up to eleven phenylene rings in the linker, and to get the isorecticular series (termed IRMOF-74-I to -XI) with the dimension of the pore apertures ranging from 14 to 98 Å.¹⁹ All members of this isorecticular series inherit the **etb** net of the parent MOF-74 topology. Also a mesoporous MOF containing a different linker (1,4-biphenyldicarboxylate, bpdc) $\text{Cd}_3(\text{bpdc})_3$ (named JUC-48, JUC – Jilin University China) with the same topology and the 1D hexagonal channels of $21 \times 25 \text{ Å}$ could be synthesised by Qiu *et al.*²⁰

A very impressive example of non-interpenetrated MOFs with tunable pore sizes is also the isorecticular series of (3,24)-connected MOFs with **rht** topology made from dendritic hexacarboxylate ligands (Table 1).

NU-110 is up to date known as the MOF with the highest pore volume. Hupp *et al.* performed a theoretical study using a hypothetical MOF constructed from 1,3,5-trisubstituted benzene with linear chains consisting of alternating single and triple bonds and ending with 3,5-dicarboxybenzene and paddlewheel units (quasi MOF isorecticular to the compounds summarized in Table 1). The authors expect that such a hypothetical material should have a BET surface area of up to $14\,600 \text{ m}^2 \text{ g}^{-1}$.³⁰

Multiligand MOFs. To combine two or more different linker molecules for the construction of MOFs seems to be quite successful strategy which increases even more the number of

Fig. 1 The influence of the synthetic conditions on the resulting phase for MOF-14 and DUT-34 systems.

Table 1 Isoreticular series of (3,24)-connected MOFs made from dendritic hexacarboxylate ligands

	Pore size (Å)	BET (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
PCN-61 ²¹	12–19	3000	1.36
PCN-66 ²¹	12–21	4000	1.63
NOTT-112 ²²	13–20	3800	1.62
PCN-68/NOTT-116 ²³	12–24	5109/4664	2.13/2.17
PCN-610/NU-100 ²⁴	12–27	n.a./6143	n.a./2.82
PCN-69 ²⁵ /NOTT-119 ²⁶	13–25	4118	2.35
NU-109 ²		7010	3.75
NU-110 ²	13–27	7140	4.4
NU-111 ^{27,28}	14–24	4930	2.09
NU-125 ²⁹	11–24	3120	1.29

possible linker–connector combinations for MOF design. In this manner a variety of mesoporous coordination polymers containing two or more linkers in the same structure could be synthesized.

A series of mesoporous compounds with exceptional porosity was obtained by combination of tritopic and ditopic carboxylic linkers, for example UCMC-1,³¹ UCMC-2,³² DUT-6³³ (MOF-205),³⁴ UCMC-3,³⁵ UCMC-4,³⁵ UCMC-5,³⁵ MOF-210,³⁴ and DUT-32.³⁶ Most of them are based on benzene-1,3,5-tribenzoate (**btb**) as the tritopic ligand and Zn₄O⁶⁺ as the SBU. According to Matzger *et al.*, for copolymerization of 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.³⁵ For the MOFs mentioned the ratios of the di- and tritopic linker (L_D/L_T) lie within the range of 0.44 to 0.66.

Combining **btb**³⁻ with tetracarboxylic ligand *N,N,N,N*-benzidinetetrabenzoate (**benztb**⁴⁻) Grnker *et al.* synthesized a Zn₄O⁶⁺ based MOF (DUT-25) with excellent porosity.³⁷

Recently, Telfer *et al.* demonstrated that the incorporation of three different linkers into a highly symmetric MOF is also possible.³⁸ Combination of Zn₄O⁶⁺, **btb**³⁻, 1,4-benzenedicarboxylate (**bdc**), 4,4'-biphenyldicarboxylate (**bpdc**) produces [Zn₄O(btb)_{4/3}(bdc)_{1/2}(bpdc)_{1/2}] (MUF-7a, MUF = Massey University Framework), which is isoreticular to DUT-6.

Bent ligands. The next strategy for the synthesis of mesoMOFs was proposed by Hong-Cai Zhou. According to it, the angular ligands can wrap around the cavities and sustain the integrity of the porous network.³⁹ Hence, PCN-21 was constructed using an angular tetratopic ligand (diphenylmethane-3,3',5,5'-tetrakis-(3,5-bisbenzoate)) in combination with Cu paddle-wheels. This MOF has a complicated porous structure with unusually large cavities up to 4 nm in diameter (Fig. 2) and a surface area as high as 4485 m² g⁻¹.

Using a bent thiophene dicarboxylic linker, namely 2,5-thiophenedicarboxylic acid (TDC) (the angle between carboxylic groups is 148.6°) in combination with ten-connecting Zr-clusters, a chemically stable MOF named DUT-68 could be obtained.⁴⁰ The complicated hierarchical pore architecture of DUT-68 contains 4 types of pores: a rhombicuboctahedral mesopore with an inner diameter of 27.7 Å, a cuboctahedral cage 13.9 Å in diameter, a square antiprism 12.5 Å in size, and smallest octahedral pores with a diameter of the inner sphere of 8 Å. Soaking DUT-68 in water does

Fig. 2 Pore windows of a cavity with an internal diameter of 40 Å (excluding van der Waals radii) in PCN-21. Reproduced from ref. 39 with permission from The Royal Society of Chemistry.

not cause changes in the powder diffraction patterns indicating its stability towards moisture. DUT-68 is also stable in the highly acidic media (conc. HCl).

MOFs from MOPs. If the angle of the bent linker allows the construction of a finite structure (for example 1,3-benzene dicarboxylate (1,3-bdc) with 120° between functional groups), large discrete molecular units, so called metal–organic polyhedra (MOPs), can be formed. From 12 paddle-wheel units bridged by 1,3-bdc a large MOP-1 could be obtained.⁴¹

Using metal–organic polyhedra (MOPs) as building blocks to design porous materials is an attractive way because it provides a high degree of control over the resulting porous structure and topology. The polyhedra serve as supramolecular building blocks (SBBs) *via* linking through multi-topic ligands. The starting metal–organic polyhedron ensures the size and geometry of the smallest pore and can be externally functionalized to connect the SBBs. Furthermore the choice of shape, size and symmetry of the molecular entity connecting the SBBs can control the number of pores as well as their shape and size. In recent years it was successfully applied to the synthesis of several (*i.e.* mesoporous) MOFs.⁴²

In 2008 Lah and co-workers⁴³ prepared an extended MOF with **rht** topology from MOP-1 by utilizing covalent bonding. They synthesized a C₃-symmetric facial ligand, which can be regarded as three 1,3-bdc moieties linked through a trigonal organic unit. The MOF contains octahedral and tetrahedral cavities 18.8 Å and 13.7 Å in diameter, respectively. Unfortunately, the adsorption properties of the MOF were not reported.

In 2008 Eddaoudi and Zaworotko also presented a MOF with a **rht**-like network based on the MOP-1 unit [(Cu₆O(TZI)₃(H₂O)₉(NO₃)]_n, TZI = 5-tetrazolyisophthalate), consisting of three different types of open cages with the largest diameter of 20.2 Å (Fig. 3).⁴⁴ The MOP-1 supermolecular building blocks (SBBs) in this structure are connected to a trigonal Cu₃O(N₄CR)₃ unit generated *in situ* during the synthesis. The apparent BET surface area was estimated to be 2847 m² g⁻¹; the total pore volume was found to be 1.01 cm³ g⁻¹.⁴⁴

Since then a plethora of highly porous isoreticular materials based on MOP-1 and C₃-symmetric ligands have been synthesised (Table 1).

Recently Kaskel *et al.* and the group of H.-C. Zhou⁴⁵ succeeded in synthesizing highly porous MOFs from cuboctahedral MOPs based on copper paddle-wheels and carbazole-3,6-dicarboxylate (Fig. 4a). The MOPs are covalently connected by a linear moiety

Fig. 3 The rhb-like network of $\text{Cu}_6\text{O}(\text{TZl})_3(\text{H}_2\text{O})_9(\text{NO}_3)$. Adapted with permission from ref. 44. Copyright (2008) American Chemical Society.

Fig. 4 (a) Carbazol-based MOP; (b) carbazol-based MOPs linked by a linear moiety in DUT-49; (c) carbazol-based MOPs linked by a 4-connecting moiety in DUT-75 and DUT-76.

(in the case of DUT-49⁴⁶ by biphenylene) to give a compound, which can be understood as an extended cubic closed packing of the cuboctahedral supramolecular building blocks (**fcu** topology, Fig. 4b). DUT-49 shows exceptionally high gravimetric methane adsorption capacity.

It was also possible to connect the same cuboctahedral metal-organic carbazole-3,6-dicarboxylate polyhedrons (acting as 12 connectors) by square planar 4-connecting units (paddle-wheels) and get a highly porous structure with **ftw** topology (Fig. 4c).⁴⁷

1.2 Post-synthetic treatment

Functionalization and post-synthetic modification. To achieve a MOF decorated with desired functional groups, a pre-functionalized organic ligand with specific functionalities can be directly used in the synthesis of the targeted compound. Mesoporous MOFs are mostly tolerant to such ligand substitution leading to a plethora of functionalized compounds, which are tuned for specific applications or can be further functionalized by a post synthetic modification (PSM) technique. PSM is defined as the chemical modification of a framework after it has been synthesized.^{48,49}

One of the mesoporous frameworks, which was extensively studied for PSM, is UMCM-1. The terephthalate in UMCM-1 can be easily substituted by aminoterephthalate and the resulting UMCM-1-NH₂ presents a platform for various chemical transformations, where the amino group serves as a chemical handle that can be manipulated *via* PSM.⁵⁰ For example, the UMCM-1-NH₂ structure was functionalized with linear alkyl chain anhydrides, branched anhydrides⁵⁰ as well as aromatic anhydrides and isocyanates.⁵¹

The UMCM-1-NH₂ was also successfully transformed with 3-hydroxyphthalic anhydride and 2,3-pyrazinedicarboxylic anhydride, for generating additional metal binding sites within a MOF. After introduction of Lewis acidic Fe³⁺ sites, the material was successfully used to catalyze the Mukaiyama-aldol reaction.⁵²

Yaghi *et al.* introduced an iminopyridine moiety into the UMCM-1 by condensation of 2-pyridinecarboxaldehyde and UMCM-1-NH₂. The iminopyridine moiety could be used for binding the Pd²⁺.⁵³

In summary, PSM is a highly versatile method which allows the incorporation of different functional groups into a MOF, which is difficult to achieve through a direct synthetic route. The mesoporosity in this case is very advantageous, since it facilitates the diffusion of reactants, catalysts, and educts to and from the reactive sites.

Ligand exchange. A fascinating technique to achieve the mesoporosity and systematically increase the pore dimension of MOFs by the elongation of linkers in a fixed topology was introduced by Rosi *et al.* The MOFs, which were difficult to synthesize directly, could be achieved by replacing the shorter ligand in a given MOF (Bio-MOF-100)⁵⁴ by a longer ligand in a crystal to crystal transformation manner.

Bio-MOF-100 consists of zinc-adeninate clusters linked by linear 4,4'-biphenyldicarboxylate (4,4'-bpdc) linkers. 4,4'-bpdc could be exchanged *in situ* by azobenzene-4,4'-dicarboxylate (giving Bio-MOF-102) or 2'-amino-1,1':4,1''-terphenyl-4,4'-dicarboxylate (giving bio-MOF-103), resulting in an increase in the pore size from 2.0 to 2.8 nm and the pore volume from 2.83 to 4.13 cc g⁻¹.⁵⁵ However, the general applicability of this concept is questionable due to the limited number of examples presented so far.

2. Characterization

2.1 Solvent removal

Efforts to achieve high nitrogen uptake for mesoporous MOFs are often hindered by the tendency of these materials to collapse upon "activation" (*i.e.* evacuation), or removal of guest molecules (solvent, linkers, or other chemicals used during the synthesis) from the MOF. Recently a substantial overview of the procedures usually applied for activation of MOFs was published by Hupp *et al.*⁵⁶ Five strategies which are effective for activating MOFs were outlined: (i) conventional heating and vacuum; (ii) solvent-exchange; (iii) supercritical CO₂ processing; (iv) freeze-drying; and (v) chemical treatment. Often the combinations of the outlined strategies need to be considered to find conditions for optimal activation of MOF.

MOFs with mesopores are in general more fragile in comparison to the microporous frameworks, and tend to collapse upon removal of guests. Supercritical CO₂ drying is often the only possibility to desolvate the mesoporous frameworks for gas adsorption purposes without network transformation.³⁶

2.2 Single crystal structure determination

The huge advantage of MOFs is their extraordinary structural variety in combination with the crystallinity, which should allow for their unambiguous structural characterization by X-ray diffraction. Determination of the single crystal structure of mesoporous MOFs, however, is often difficult or impossible by the use of conventional laboratory X-ray instrumentation. The crystals of MOFs are often small, very sensitive to moisture and solvent loss, contain mainly organic matter, and most

importantly, contain huge cavities filled with disordered solvent molecules. All these factors contribute to the low resolution and signal-to-noise ratio, as well as to low data quality needed for satisfying structure refinement. Therefore, the data collection at the synchrotron seems to be ideal to provide high quality diffraction data for structure refinement of (mesoporous) metal-organic frameworks. Thus, the structure of PCN-21³⁹ and the structures of a lot of Zr based MOFs^{57–60} could be solved only from data collected using synchrotron radiation. Very often, a combinational approach using X-ray crystallography and a structural modeling should be applied to build the structure of highly porous MOF, or to identify the position of the linker substituents.^{15,34,61}

The knowledge of the crystal structure allows the precise determination of the active site (catalytic active centres, chiral groups *etc.*) as well as pore sizes.⁶² Often the crystal structure is used for calculation of so called geometrical surface area.⁶³ However, one should keep in mind that (i) the determination of the crystal structure is usually performed for solvated compound and the structure could (slightly) change after activation; (ii) the structure can be influenced by the temperature, since most of the diffraction measurements are performed either at room temperature or at low temperature (usually 100 K). An example for the case (i) is the inconsistency in the pore window size determined crystallographically with the adsorption behaviour of ZIF-8.⁶⁴ The compound adsorbs molecules larger than expected,⁶⁵ which could be explained by the motion/rotation of linker molecules.

The reports on the temperature dependent structure changes are very rare,⁶⁶ and the phenomenon should be investigated more in detail.

For example, the framework of DUT-7 at room temperature (RT) has the composition $\text{Zn}_4\text{O}((\text{S})\text{-L})_3$ ((S)-L = (S)-2,2'-spirobiindane-5,5'-dicarboxylate) and crystallizes in the space group $P6_322$. A reversible structural transformation was observed upon cooling to 100 K during single crystal X-ray diffraction measurement. The resulting low temperature structure is characterized by a Zn_4O^{6+} cluster not only coordinated by six linker moieties but also by two additional solvent molecules leading to an octahedral coordination of one of the zinc ions of the cluster (Fig. 5). This structure transformation leads to a tripled unit cell compared to DUT-7(RT) and a change of the space group to $P6_522$.⁶⁷

Fig. 5 (a) Secondary building units of DUT-7(RT) and (b) DUT-7(LT), both: view along [001]. Reprinted with permission from ref. 67. Copyright (2010) American Chemical Society.

DUT-28 ($\text{Co}_{22}(\text{BTB})_{12}(\text{NO}_3)_8(\text{DEF})_x(\text{H}_2\text{O})_y$) adopts the space group $C2/m$ at room temperature. Interestingly, the structure shows a strong temperature induced transformation at 100 K. At low temperature, the space group is changed to $C2/c$ (DUT-28(LT)) and a cell volume decrease of 9% is observed.⁶⁸

2.3 Textural properties

BET surface area, geometrical surface area and apparent surface area. Evaluation of textural properties is crucial for porous solids, because they are decisive for specific impact on the performance of the materials in adsorption applications. For micro/mesoporous materials such characteristics are usually the specific surface area, micropore and mesopore volume, as well as pore size distribution. They are usually derived from the nitrogen (or argon) adsorption isotherm measured at 77 (87) K. Especially for pore size distribution analysis, argon adsorption is recommended.

Metal-organic frameworks, due to their crystallinity, provide unique opportunities in contrast to non-ordered porous solids, to determine all ideal textural parameters geometrically from the crystal structure. The measured and calculated values can be compared more or less directly, to ensure the quality of the synthesized and activated sample. While the estimation of pore volume is appropriate, the determination of specific surface area from measured isotherms is critical. In some older publications even Langmuir surface areas are reported which is meaningless and inappropriate. In several publications on MOFs, the BET areas are commonly reported as specific surface areas, although in the proper meaning of the BET theory, it is not applicable to microporous materials. In the meantime, several studies or commentaries in the literature on the applicability of the BET theory to zeolites and, in recent years, to MOFs were published. For example, Snurr *et al.* have shown that for MOFs and zeolites containing “ultra-micropores” ($<7 \text{ \AA}$), the BET surface areas calculated from simulated nitrogen or argon isotherms agree well with the accessible surface areas obtained directly from crystal structures if the BET analysis is performed within the appropriate pressure range (*i.e.* lower than for meso- or non-porous solids) based on published consistency criteria.⁶⁹ However, BET analysis of microporous materials only provides an apparent surface area reflecting the number of molecules with the strongest interaction (“first monolayer”) which is not exactly identical to the calculated accessible geometric surface area.

Even more complications are met when it comes to MOFs with multimodal pore size distributions with sizes ranging from the micropore to the mesopore regime. In this case, stepwise adsorption results caused by first filling the micropores with adsorbates, followed by adsorption along the mesopore walls, and finally filling of mesopores.⁷⁰ Such a behavior is almost always observed for MOFs with extremely high surface area due to the hierarchical and multimodal pore architecture.

The accepted protocol for extracting a specific surface area from the sorption data of a given compound starts with the BET-plot of the adsorption isotherm.⁷¹ The BET-plot

is derived from the linear form of the BET equation (eqn (1)):

$$\frac{p/p_0}{n(1-p/p_0)} = \frac{1}{n_m} + \frac{C-1}{n_m C} (p/p_0) \quad (1)$$

where $\frac{p/p_0}{n(1-p/p_0)}$ (p – pressure, p_0 – vapor pressure of the used adsorptive at the indicated temperature, n – specific amount adsorbed at the relative pressure p/p_0 (STP), n_m – the monolayer capacity, C – constant) is plotted as a function of the relative pressure p/p_0 .

First of all, a linear range in the BET-plot should be identified. From the linear equation fitted to this range of the experimental data one can extract the monolayer capacity (n_m) for the given compound. Subsequent multiplication of the cross-sectional area of the adsorptive molecules with the monolayer capacity and Avogadro constant provides the BET area (or specific BET area, when divided by the mass of the adsorbent) for the compound in question. This analysis routine is implemented in the software of most adsorption analysis equipment manufacturers. However, a challenge is to identify the appropriate linear range for the application of the BET theory. The initially suggested range by Brunauer, Emmet and Teller from 0.05 to 0.3 relative pressures is only applicable to non-porous or mesoporous materials (if the condensation is not in this range) and cannot be applied for MOFs with multimodal pore size distribution. For choosing the appropriate range for analysis, Rouquerol and Llewellyn suggested a set of rules (consistency criteria) which the chosen pressure range should comply with.⁷²

(1) The analysis should be limited to the range in which the term $n(1 - p/p_0)$ increases continuously as a function of the relative pressure p/p_0 .

(2) The value of the BET constant C resulting from the linear fit should be positive. To give meaningful results the C constant should have a value of at least 10.

(3) The BET monolayer capacity n_m calculated from the linear fit corresponds to a certain relative pressure, which must be located within the linear region chosen for the area calculation.

As an illustrative example, we would like to discuss the problems of applying the consistency criteria and estimation of BET area for the highly porous material $\text{Zn}_4\text{O}(\text{bpdc})(\text{btctb})_{4/3}$, further denoted as DUT-32 (btctb – 4,4',4''-[benzene-1,3,5-triyl-tris(carbonylimino)]trisbenzoate, bpdc – 4,4'-biphenyldi-carboxylate).³⁶ DUT-32 is a 3D framework with three different 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. 6).

Application of the first criterion limits the range of the BET plot to a relative pressure of 0.21 (Fig. 7).

Because this criterion is implemented nowadays in the software of adsorption equipment it is widely used. Within this range of the BET plot for DUT-32 one can find eight (!) different linear ranges with positive C constants, all of them having a C constant of 10 or higher, thus satisfying the first and second criterion.

Fig. 6 Four different pores within the structure of DUT-32. Reproduced from ref. 36 with permission from The Royal Society of Chemistry.

Fig. 7 $V(1 - p/p_0)$ vs. p/p_0 for DUT-32. Reproduced from ref. 36 with permission from The Royal Society of Chemistry.

Fig. 8 shows the full BET plot with the different regions marked in different colors with the corresponding linear regressions, the calculated C constants and the resulting BET areas. Applying only the first two criteria which are usually used in determining specific surface areas by the MOF community, BET areas for DUT-32 ranging from $5\,699 \text{ m}^2 \text{ g}^{-1}$ up to $10\,392 \text{ m}^2 \text{ g}^{-1}$ can be calculated.

Is the DUT-32 a material with ultrahigh porosity breaking a world record in terms of surface area? For an unambiguous selection of the right BET range an often neglected third consistency criterion suggested by Rouquerol and Llewellyn has to be considered: calculation of the relative pressure corresponding to a given monolayer capacity n_m .

$$\left(\frac{p}{p_0}\right)_{n_m} = \frac{1}{\sqrt{C} + 1} \quad (2)$$

Fig. 8 BET plot of the N_2 isotherm (77 K); colored points within the plot illustrate different possible linear regions for the estimation of the BET specific surface area. Reproduced from ref. 36 with permission from The Royal Society of Chemistry.

The test if the relative pressure $\left(\frac{p}{p_0}\right)_{n_m}$ which corresponds to the monolayer capacity for DUT-32 is located within the chosen relative pressure range of the linear region of BET plot narrows the list to only one linear range. Only the linear fit in the pressure range $0.0982 \leq p/p_0 \leq 0.1323$ with a C constant of 43.32 ($p/p_0(n_m) = 0.132$) meets all the requirements listed above, suggesting that the consistent approximation of the BET area for DUT-32 is $6411 \text{ m}^2 \text{ g}^{-1}$. It should be mentioned that the third criterion was not considered and is not fulfilled for NU-109 and NU-110, currently published world record materials with the highest BET areas estimated using only two consistency criteria. Nevertheless, with the huge pore volumes of $3.75 \text{ cm}^3 \text{ g}^{-1}$ for NU-109 and $4.40 \text{ cm}^3 \text{ g}^{-1}$ for NU-110 these two MOFs are record coordination polymers regarding the specific total pore volume.

The geometrical surface area of DUT-32 calculated using the Poreblazer V1.2 program is $5981 \text{ m}^2 \text{ g}^{-1}$.

The deviation is caused by the different physical meaning of the apparent BET surface area and the geometrical surface area which do not need to match each other (see above).

Hysteresis and structure transformations during gas adsorption. Sometimes, the elongation of linker molecules has a pronounced effect on the behavior during the adsorption and on the isotherm shape.

For PCN-69 (Table 1), steps in oxygen adsorption isotherms (Fig. 10) were attributed to the pressure-responsive linker geometry changes.

Namely, adsorbing O_2 triggers the conformation change of btti (Fig. 9) from a bent ligand to a stretched one.

An unusual adsorption behavior was observed for $\text{Zn}_4\text{O}(\text{BenzTB})_{3/2}$ (DUT-13, $\text{BenzTB}^{4-} = N,N',N'',N'''$ -benzidine-tetra-benzoate)⁷³ based on a quite long and conformational flexible linker. The compound has corundum topology (cor) and largest pores $29.4 \times 19 \text{ \AA}$ in diameter (van der Waals radii of corresponding atoms have been considered).

The pronounced step in the isotherm was observed during the adsorption of N_2 (at 77 K) (Fig. 11), CO_2 (at 195 K) and $n\text{-C}_4\text{H}_{10}$ (at 293 K). The stepwise uptake is very typical for flexible (so called breathing) MOFs, where the increased pressure causes the pore opening and the increase of the surface area and the pore volume. The origin of the hysteresis in DUT-13 is not fully understood so far.

By repeating the N_2 adsorption experiment using the same DUT-13 sample the hysteresis loop becomes narrow ending up in a type I like isotherm.

Fig. 9 Conformation of the btti linker in PCN-69. Adapted with permission from ref. 25. Copyright (2011) American Chemical Society.

Fig. 10 Gas physisorption isotherms of PCN-69 (a) O_2 at 77 K; (b) CO_2 at 195 K. Adapted with permission from ref. 25. Copyright (2011) American Chemical Society.

Fig. 11 N_2 physisorption isotherms of DUT-13 at 77 K: 1st run (adsorption/desorption $\bullet/\circ$), 2nd run (adsorption/desorption $\blacktriangle/\triangle$) and 3rd run (adsorption/desorption $\blacklozenge/\lozenge$). The huge hysteresis loop decreases with run to run and the isotherm approximates type I. Reproduced from ref. 73 with permission from The Royal Society of Chemistry.

Interestingly, the adsorption of supercritical gases such as hydrogen and methane at high pressures does not induce the hysteretic behavior and does not change the isotherm during cycling.

This behavior points towards the strong surface tension effects during subcritical adsorption which can cause deformation of the structure. The latter is more important in MOFs that are crystalline solids with a narrow pore size distribution as compared to classical mesoporous materials because the tension forces act simultaneously when the pore is filled.

3. High pressure gas adsorption

It is widely accepted that high internal surface area, large pore volume and strong energetic interactions between the framework and the gas molecules are highly beneficial for enhancing the gas storage capacity.^{74,75}

Especially in the moderate to high pressure regime the interplay of pore volume and desired storage pressure is important. Under such storage conditions, mesoporous MOFs are beneficial due to the rising contribution of compressed gas in the free pore volume of the MOF at higher pressure.

Since the MOFs with the highest porosity often have very low crystalline density, they lose in competition with high density compounds, if the high volume-based adsorption capacity is needed.

For practical applications also the so called working pressure range must be taken into account (the lower boundary of

pressure tolerated by the engine system) as well as the principal differences in the excess, total, absolute and deliverable/usable capacity. The article recently published by J. Long *et al.* nicely summarises the important key points to be considered for the natural gas storage using MOFs.⁷⁶ The authors claim that efforts to minimize the amount of wasted volume not contributing to optimally attracting CH₄ molecules is essential, without significantly decreasing the porosity.

According to our work the differences in the storage performance of microporous and mesoporous materials can be used to avoid the free space in the storage cylinder for improved storage performance, for example using HKUST-1⁷⁷ and MIL-101(Cr)⁷⁸ in combination.

The experimental setup constructed and used by us for measuring the deliverable amount of gas is a model miniature tank system. The scalability of the obtained results was proven by using 4 ml, 25 ml and 5 L sample containers. In a typical experiment, the tank was completely filled with an activated adsorbent, the 200 bar methane was introduced at 293 K and the delivered amount was monitored upto 1 bar (ambient pressure) during the desorption. This amount could be directly compared with the amount delivered from a cylinder itself and represents the effective storage amount.⁷⁹

The density of a packed powder can considerably influence the effective storage amount. The simplest way to enhance the packing density is to press the MOF into pellets. But mechanical stress often leads to the decrease of the porosity and consequently, the storage capacity of the MOF.^{80,81} This is also the case for HKUST-1 and MIL-101(Cr).⁸¹ The packing density of HKUST-1 and MIL-101 powder is 0.52 g cm⁻¹ and 0.28 g cm⁻¹, respectively. The ideal crystal density of HKUST-1 and MIL-101 (without solvent molecules) is 0.88 g cm⁻¹ and 0.44 g cm⁻¹, respectively. Consequently, approximately 41% (for HKUST-1) and accordingly 36% (for MIL-101) of the space of the tank is not occupied by the MOF. To improve the situation we decided to combine these two MOFs in the following way: the 40% free space of HKUST-1 should be filled with nanocrystalline MIL-101. Therefore to fill 1 ml space in the tank a mixture containing 0.52 g HKUST-1 and 0.11 g MIL-101(Cr) was used.

The improvement achieved using the combination of two different porous coordination polymers depends on the pressure region. Since the mesoporous MOF was added to the

microporous one, the highest gain is achieved in the high pressure region (Fig. 12).

In Europe, existing natural gas filling stations operate at 200 bar, and thus increasing the storage capacity at high pressure is essential for a competitive commercialization of adsorbed natural gas (ANG) driven cars. The combination of different MOFs with synergetic characteristics enhances the adsorption performance of the system and allows tuning in the desired pressure range as well as to minimize the amount of empty, intercrystalline void volume in the storage tank.

4. Adsorption in the liquid phase

Since the problem of proper desolvation of the metal-organic frameworks appears quite often by the compounds including large mesopores, the application of such MOFs as adsorbents in the liquid phase is a very promising direction.

However, in comparison to the plethora of investigations carried out on gas separation, gas adsorption, and catalytic reactions using MOFs, the studies on adsorption/separation in the liquid phase are underrepresented in the literature and much more research is needed in this field, since many applications (such as separation or heterogeneous catalysis) require adsorption data in solutions.

Mesoporous MOFs often display adequate pore and pore window size for adsorption of large organic molecules, as well as acceptable guest exchange kinetics, making mesoporous MOFs very promising candidates for separation applications in the liquid phase.

It was already shown that MOFs can effectively adsorb large quantities of organosulfur, aromatic, and chloroaromatic compounds.^{82–84}

Yan *et al.* have used MIL-101(Cr)⁷⁸ as an HPLC stationary phase for separation of C₆₀ and C₇₀. Not only high resolution separation was observed, but also the baseline separation of other high fullerenes, such as C₇₆, C₇₈, C₈₂, C₈₄, C₈₆ and C₉₆, showing that MOFs can be used as advanced media for the separation of large, even very hydrophobic molecules such as fullerenes. The separation succeeds at room temperature within a short separation time (only 3 min) with a selectivity of C₇₀/C₆₀ = 17 and a column efficiency of 1.3 × 10⁴ plates per m for C₇₀. The MIL-101(Cr)-packed column also offered efficient separation of high-order fullerenes (*e.g.*, C₇₀, C₇₆, C₇₈, and C₈₂). This outstanding selectivity can be attributed to the differences in their solubility in the mobile phase, adsorption on the outer surface of the MIL-101(Cr), and π - π and van der Waals interactions between those fullerenes and MIL-101(Cr).

Xu *et al.* applied Zn₄O(L)_{1.5} (L = 6,6'-(2,2-bis((6-carboxynaphthalen-2-yloxy)methyl)propane-1,3-diyl)bis(oxy)di-2-naphthalenecarboxylate) with corundum-type frameworks and hierarchical pore sizes (16.1, 18.6 and 38.3 Å) as a column-chromatographic filler for separation of large dye molecules. Two dyes of basic red 1 and food green 3 could be successfully separated by size exclusion mechanisms. The larger food green 3 cannot be adsorbed by the MOF and is rapidly transported through the column along with the solvent stream while the adsorbed basic red 1 is retained

Fig. 12 Methane desorption isotherms at 293 K for MIL-101(Cr) (green), HKUST-1 (blue), and MIL-101(Cr)-HKUST-1 mixture (orange). The red line represents the amount delivered by not filled cylinder itself.

inside the MOF cages for longer time, thus resulting in the separation, which was not only observable by the naked eye but was also confirmed by UV-vis spectra of the eluent.⁸⁵

Enantioselective separation was performed for the first time by Kaskel *et al.* on a chiral modified UCMCM-1 analogue, which has mesoporous channels. Bn-ChirUCMCM-1⁶¹ was used as the stationary phase for high-performance liquid chromatography. 1-Phenylethanol as the analyte showed both selective and enantioselective interactions with the MOF. The potential for enantioseparation can be clearly seen from the selectivity, which is high enough to reach enantiomer separation, however, so far the resolution was too small to reach peak separation under the chosen conditions.

5. Conclusions

Mesoporous MOFs are nowadays the materials with the highest specific surface area known and show high adsorption capacities for small molecules but are also important solids for liquid phase separation and chromatography.

Despite the excellent porosity, mesoporous MOFs have several unique properties, such as crystallinity, flexibility, and crystallographically defined position of functional groups, which allows a precise tuning of such materials for specific tasks. However, the synthesis of large pore MOFs is often limited by the solubility and synthesis of the corresponding organic linkers, the latter being very often quite complex (intensive knowledge in preparative organic chemistry is needed), time consuming (multi-step synthesis and protective group chemistry, complex separation and purification), expensive (noble metals like palladium are required as catalysts), with low overall reaction yields. As a result, the scale-up of these MOFs is challenging. Also the solvents usually used in the synthesis of MOFs are not easy to handle, and more research has to be devoted to “green” synthetic conditions.

Consistent determination of apparent BET surface areas is important and standards should be established making BET surface areas better comparable for mesoporous MOFs.

The concepts for rational design are well established and thus it is essential to focus on a better understanding of the dynamic properties of such solids. The labile structure can cause distortions in the linker and also the cluster system during the adsorption, thermal action, or chemical reactions leading to reversible or irreversible structural changes which are yet to be investigated in more detail. Adjusting the topology and composition, formulation and functionalization provides a rich basis for the design of customized materials and realization of a wide variety of chemical and physical functions, a wide open field for exploration.

Acknowledgements

The authors would like to thank Dr Nicole Klein, Dr Ronny Grunker and Dr Ulrich Stoeck for very enjoyable collaboration and fruitful scientific discussions.

Notes and references

- 1 L. Sarkisov, *Adv. Mater.*, 2012, **24**, 3130.
- 2 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. . Yazaydin, *J. Am. Chem. Soc.*, 2012, **134**, 15016.
- 3 M. Fernandez, T. K. Woo, C. E. Wilmer and R. Q. Snurr, *J. Phys. Chem. C*, 2013, **117**, 7681.
- 4 E. M. Renkin, *J. Gen. Physiol.*, 1954, **38**, 225.
- 5 N. Stock and S. Biswas, *Chem. Rev.*, 2012, **112**, 933.
- 6 M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O’Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469.
- 7 H.-L. Jiang, T. A. Makal and H.-C. Zhou, *Coord. Chem. Rev.*, 2013, **257**, 2232.
- 8 O. Shekhah, H. Wang, M. Paradinas, C. Ocal, B. Schuepbach, A. Terfort, D. Zacher, R. A. Fischer and C. Woell, *Nat. Mater.*, 2009, **8**, 481.
- 9 S. R. Batten, S. M. Neville and D. R. Turner, *Coordination Polymers: Design, Analysis and Application*, Cambridge, 2009.
- 10 B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.
- 11 S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148.
- 12 B. Chen, M. Eddaoudi, S. T. Hyde, M. O’Keeffe and O. M. Yaghi, *Science*, 2001, **291**, 1021.
- 13 S. Ma, D. Sun, M. Ambrogio, J. A. Fillinger, S. Parkin and H.-C. Zhou, *J. Am. Chem. Soc.*, 2007, **129**, 1858.
- 14 S. Ma, D. Sun, M. Ambrogio, J. A. Fillinger, S. Parkin and H.-C. Zhou, *J. Am. Chem. Soc.*, 2007, **129**, 1858.
- 15 N. Klein, I. Senkovska, I. A. Baburin, R. Grunker, U. Stoeck, M. Schlichtenmayer, B. Streppel, U. Mueller, S. Leoni, M. Hirscher and S. Kaskel, *Chem. – Eur. J.*, 2011, **17**, 13007.
- 16 K. Gedrich, M. Heitbaum, A. Notzon, I. Senkovska, R. Frhlich, J. Getzschmann, U. Mueller, F. Glorius and S. Kaskel, *Chem. – Eur. J.*, 2011, **17**, 2099.
- 17 N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O’Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 1504.
- 18 P. D. C. Dietzel, B. Panella, M. Hirscher, R. Blom and H. Fjellvg, *Chem. Commun.*, 2006, 959.
- 19 H. Deng, S. Grnder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gndara, A. C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O’Keeffe, O. Terasaki, J. F. Stoddart and O. M. Yaghi, *Science*, 2012, **336**, 1018.
- 20 Q.-R. Fang, G.-S. Zhu, Z. Jin, Y.-Y. Ji, J.-W. Ye, M. Xue, H. Yang, Y. Wang and S.-L. Qiu, *Angew. Chem., Int. Ed.*, 2007, **46**, 6638.
- 21 D. Yuan, D. Zhao, D. Sun and H.-C. Zhou, *Angew. Chem., Int. Ed.*, 2010, **49**, 5357.
- 22 Y. Yan, X. Lin, S. Yang, A. J. Blake, A. Dailly, N. R. Champness, P. Hubberstey and M. Schroder, *Chem. Commun.*, 2009, 1025.
- 23 Y. Yan, I. Telepeni, S. Yang, X. Lin, W. Kockelmann, A. Dailly, A. J. Blake, W. Lewis, G. S. Walker, D. R. Allan, S. A. Barnett, N. R. Champness and M. Schrder, *J. Am. Chem. Soc.*, 2010, **132**, 4092.
- 24 O. K. Farha, A. . 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.
- 25 D. Yuan, D. Zhao and H.-C. Zhou, *Inorg. Chem.*, 2011, **50**, 10528.
- 26 Y. Yan, S. Yang, A. J. Blake, W. Lewis, E. Poirier, S. A. Barnett, N. R. Champness and M. Schroder, *Chem. Commun.*, 2011, **47**, 9995.
- 27 Y. Peng, G. Srinivas, C. E. Wilmer, I. Eryazici, R. Q. Snurr, J. T. Hupp, T. Yildirim and O. K. Farha, *Chem. Commun.*, 2013, **49**, 2992.
- 28 O. K. Farha, C. E. Wilmer, I. Eryazici, B. G. Hauser, P. A. Parilla, K. O’Neill, A. A. Sarjeant, S. T. Nguyen, R. Q. Snurr and J. T. Hupp, *J. Am. Chem. Soc.*, 2012, **134**, 9860.
- 29 C. E. Wilmer, O. K. Farha, T. Yildirim, I. Eryazici, V. Krungleviciute, A. A. Sarjeant, R. Q. Snurr and J. T. Hupp, *Energy Environ. Sci.*, 2013, **6**, 1158.
- 30 O. K. Farha, I. Eryazici, N. C. Jeong, B. G. Hauser, C. E. Wilmer, A. A. Sarjeant, R. Q. Snurr, S. T. Nguyen, A. A. . Yazaydin and J. T. Hupp, *J. Am. Chem. Soc.*, 2012, **134**, 15016.
- 31 K. Koh, A. G. Wong-Foy and A. J. Matzger, *Angew. Chem., Int. Ed.*, 2008, **47**, 677.
- 32 K. Koh, A. G. Wong-Foy and A. J. Matzger, *J. Am. Chem. Soc.*, 2009, **131**, 4184.
- 33 N. Klein, I. Senkovska, K. Gedrich, U. Stoeck, A. Henschel, U. Mueller and S. Kaskel, *Angew. Chem., Int. Ed.*, 2009, **48**, 9954.

- 34 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.
- 35 K. Koh, A. G. Wong-Foy and A. J. Matzger, *J. Am. Chem. Soc.*, 2010, **132**, 15005.
- 36 R. Grünker, V. Bon, P. Muller, U. Stoeck, S. Krause, U. Mueller, I. Senkovska and S. Kaskel, *Chem. Commun.*, 2014, **50**, 3450.
- 37 R. Grünker, V. Bon, A. Heerwig, N. Klein, P. Muller, U. Stoeck, I. A. Baburin, U. Mueller, I. Senkovska and S. Kaskel, *Chem. – Eur. J.*, 2012, **18**, 13299.
- 38 L. Liu, K. Konstas, M. R. Hill and S. G. Telfer, *J. Am. Chem. Soc.*, 2013, **135**, 17731.
- 39 W. J. Zhuang, S. Q. Ma, X. S. Wang, D. Q. Yuan, J. R. Li, D. Zhao and H. C. Zhou, *Chem. Commun.*, 2010, **46**, 5223.
- 40 V. Bon, I. Senkovska, I. A. Baburin and S. Kaskel, *Cryst. Growth Des.*, 2013, **13**, 1231.
- 41 M. Eddaoudi, J. Kim, J. B. Wachter, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2001, **123**, 4368.
- 42 J. J. Perry IV, J. A. Perman and M. J. Zaworotko, *Chem. Soc. Rev.*, 2009, **38**, 1400.
- 43 Y. Zou, M. Park, S. Hong and M. S. Lah, *Chem. Commun.*, 2008, 2340.
- 44 F. Nouar, J. F. Eubank, T. Bousquet, L. Wojtas, M. J. Zaworotko and M. Eddaoudi, *J. Am. Chem. Soc.*, 2008, **130**, 1833.
- 45 W. Lu, D. Yuan, T. A. Makal, Z. Wei, J.-R. Li and H.-C. Zhou, *Dalton Trans.*, 2013, **42**, 1708.
- 46 U. Stoeck, S. Krause, V. Bon, I. Senkovska and S. Kaskel, *Chem. Commun.*, 2012, **48**, 10841.
- 47 U. Stoeck, S. Krause, V. Bon, I. Senkovska, S. Kaskel, 2014, submitted.
- 48 K. K. Tanabe and S. M. Cohen, *Chem. Soc. Rev.*, 2011, **40**, 498.
- 49 S. M. Cohen, *Chem. Rev.*, 2012, **112**, 970.
- 50 Z. Wang, K. K. Tanabe and S. M. Cohen, *Inorg. Chem.*, 2008, **48**, 296.
- 51 Z. Wang, K. K. Tanabe and S. M. Cohen, *Chem. – Eur. J.*, 2009, **16**, 212.
- 52 K. K. Tanabe and S. M. Cohen, *Angew. Chem., Int. Ed.*, 2009, **48**, 7424.
- 53 C. J. Doonan, W. Morris, H. Furukawa and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 9492.
- 54 J. An, O. K. Farha, J. T. Hupp, E. Pohl, J. I. Yeh and N. L. Rosi, *Nat. Commun.*, 2012, **3**, 604.
- 55 T. Li, M. T. Kozlowski, E. A. Doud, M. N. Blakely and N. L. Rosi, *J. Am. Chem. Soc.*, 2013, **135**, 11688.
- 56 J. E. Mondloch, O. Karagiari, O. K. Farha and J. T. Hupp, *Crys-tEngComm*, 2013, **15**, 9258.
- 57 V. Bon, I. Senkovska, I. A. Baburin and S. Kaskel, *Cryst. Growth Des.*, 2013, **13**, 231.
- 58 V. Bon, V. Senkovskyy, I. Senkovska and S. Kaskel, *Chem. Commun.*, 2012, **48**, 8407.
- 59 V. Bon, I. Senkovska, M. S. Weiss and S. Kaskel, *CrystEngComm*, 2013, **15**, 9572.
- 60 S. Biswas, M. Grzywa, H. P. Nayek, S. Dehnen, I. Senkovska, S. Kaskel and D. Volkmer, *Dalton Trans.*, 2009, 6487.
- 61 M. Padmanaban, P. Muller, C. Lieder, K. Gedrich, R. Grünker, V. Bon, I. Senkovska, S. Baumgartner, S. Opelt, S. Paasch, E. Brunner, F. Glorius, E. Klemm and S. Kaskel, *Chem. Commun.*, 2011, **47**, 12089.
- 62 E. L. First and C. A. Floudas, *Microporous Mesoporous Mater.*, 2013, **165**, 32.
- 63 L. Sarkisov and A. Harrison, *Mol. Simul.*, 2011, **37**, 1248.
- 64 K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 10186.
- 65 A. Henschel, I. Senkovska and S. Kaskel, *Adsorption*, 2011, **17**, 219.
- 66 M. Wriedt, A. A. Yakovenko, G. J. Halder, A. V. Prosvirin, K. R. Dunbar and H.-C. Zhou, *J. Am. Chem. Soc.*, 2013, **135**, 4040.
- 67 K. Gedrich, I. Senkovska, I. A. Baburin, U. Mueller, O. Trapp and S. Kaskel, *Inorg. Chem.*, 2010, **49**, 4440.
- 68 P. Wollmann, M. Leistner, U. Stoeck, R. Grünker, K. Gedrich, N. Klein, O. Throl, W. Grahler, I. Senkovska, F. Dreisbach and S. Kaskel, *Chem. Commun.*, 2011, **47**, 5151.
- 69 T. Düren, F. Millange, G. Férey, K. S. Walton and R. Q. Snurr, *J. Phys. Chem. C*, 2007, **111**, 15350.
- 70 D. Yuan, R. B. Getman, Z. Wei, R. Q. Snurr and H.-C. Zhou, *Chem. Commun.*, 2012, **48**, 3297.
- 71 D. H. E. K. S. W. Sing, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol and T. Siemieniowska, *Pure Appl. Chem.*, 1985, **57**, 603.
- 72 P. L. Llewellyn, F. Rodriguez-Reinoso, J. Rouquerol and N. Seaton, *Studies in Surface Science and Catalysis*, Elsevier, 2007, p. 49.
- 73 R. Grünker, I. Senkovska, R. Biedermann, N. Klein, M. R. Lohe, P. Muller and S. Kaskel, *Chem. Commun.*, 2011, **47**, 490.
- 74 T. Düren, L. Sarkisov, O. M. Yaghi and R. Q. Snurr, *Langmuir*, 2004, **20**, 2683.
- 75 H. Furukawa and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 8875.
- 76 J. A. Mason, M. Veenstra and J. R. Long, *Chem. Sci.*, 2014, **5**, 32.
- 77 S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148.
- 78 G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble and I. Margiolaki, *Science*, 2005, **309**, 2040.
- 79 I. Senkovska and S. Kaskel, *Microporous Mesoporous Mater.*, 2008, **112**, 108.
- 80 Y. Peng, V. Krungleviciute, I. Eryazici, J. T. Hupp, O. K. Farha and T. Yildirim, *J. Am. Chem. Soc.*, 2013, **135**, 11887.
- 81 C. Montoro, F. Linares, E. Quartapelle Procopio, I. Senkovska, S. Kaskel, S. Galli, N. Masciocchi, E. Barea and J. A. R. Navarro, *J. Am. Chem. Soc.*, 2011, **133**, 11888.
- 82 K. A. Cychoz, A. G. Wong-Foy and A. J. Matzger, *J. Am. Chem. Soc.*, 2008, **130**, 6938.
- 83 H.-Y. Kim, S.-N. Kim, J. Kim and W.-S. Ahn, *Mater. Res. Bull.*, 2013, **48**, 4499.
- 84 A. Henschel, I. Senkovska and S. Kaskel, *Adsorption*, 2011, **17**, 219.
- 85 Y.-Q. Lan, H.-L. Jiang, S.-L. Li and Q. Xu, *Adv. Mater.*, 2011, **23**, 5015.