Functional group tolerance in BTB-based metal–organic frameworks (BTB – benzene-1,3,5-tribenzoate)

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ABSTRACT
The effect of different substituents on the structural tolerance of benzene-1,3,5-tribenzoate (BTB) based MOFs was studied. For this purpose, three new BTB derivatives ((NH2)3-BTB, tri((tert-butoxycarbonyl)-amino)-BTB; tri((S)-2-acetoxy-2-phenylacetamido)-BTB) were synthesized and utilized in MOF synthesis using synthetic conditions established for eight known MOFs. Three new isoreticular compounds (NH2-DUT-6, NHBoc-DUT-25, mand-DUT-25) could be identified. Furthermore, two compounds with network topologies differing from the parent compound comprising NHBoc-BTB and Cu-paddlewheels as nodes were found: Cu2(H2O)2(H(NHBoc)-BTB)2(H2O)2 (I), a dense structure containing layers with sql topology, and Cu3(H2O)(NH-Boc-BTB)2(bipy) (bipy – 4,4'-bipyridine, DUT-109), with crosslinked iab-network. The porosity of DUT-109 was proven by liquid phase adsorption of ethyl cinnamate from n-heptane. In general, a significant influence of the BTB substituent on the framework formation could be demonstrated.

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1. Introduction

Metal-organic frameworks (MOFs) offer an intriguing concept for the modular design of functional porous materials [1]. By varying the interconnection of inorganic nodes (metal atoms or metal-oxo-clusters) and organic linkers (typically polycarboxylates) a plethora of 3D frameworks with various topologies and textural properties, pore accessibility as well as chemical properties of their inner surface could be formed [2]. Therefore, a lot of applications can be envisioned with specifically tailored adsorbents, including gas storage [3,4], gas capture [5,6], separation applications [7], catalysis [8,9], and sensing [10]. However, for specific applications, additional functionalization of the framework is often required in order to achieve the targeted properties. Realizing such specific functionalities of MOF inner surface remains a challenge. In this regard, several approaches for MOF functionalization were developed so far. The first and simplest one, namely isoreticular synthesis, allows for variation of the chemical functionality of the organic linker while maintaining the desired framework topology. It is a useful concept to precisely tune the chemical properties of a given coordination polymer. Initially introduced by Yaghi and co-workers with the IRMOF series [11], it has been successfully applied several times, resulting in intriguing compounds combining the topology and porosity of the parent MOF with an adjustable inner surface functionality. With the abundance of MOFs and functional groups at hand, the variation and manipulation of chemical properties of MOFs by means of isoreticular synthesis remains fascinating. However, this “model-kit” concept for introducing functional groups into known MOF structures has some limitations: (i) A number of useful functional groups are not stable under the typically applied solvothermal synthetic conditions of MOFs [12]; (ii) Due to sterical demand, frameworks with different topologies can be formed [13]; or (iii) side reactions [12], proceeding in the synthesis mixture, can perturb the formation of an isoreticular product. So far, such effects are generally not completely predictable [14]; therefore the compatibility of a given functionalized linker with a specific MOF synthesis requires additional experimental investigations.
Another powerful approach to functionalize MOFs is the post-synthetic introduction of functional groups using the original framework bearing an anchoring group [15]. Many postsynthetic modifications (PSM) were performed with amino functionalized linkers as they have been shown to tolerate various synthesis conditions and enabled isoreticular synthesis in many cases.

Several modifications were performed on MOFs containing commercially available amino-terephthalate (NH2-BDC), such as MOF-5 [11], UMCM-1 and DMOF-1 [16], MIL-101(Fe) [17], and UiO-66 [18]. In order to incorporate amino-modified bipyridylcarboxylate (NH2-BPDC) into the corresponding IRMOF-9, the amino function had to be protected with a tert-butylxycarbonyl (Boc) protecting group [19]. Amino-functionalized benzene tricarboxylic acid (H3(NH2-BTBC)) was synthesized by Fröba and co-workers with further successful utilization in the synthesis of an HKUST-1 analog [20].

However, for most of the MOFs composed of the linear NH2-BDC linkers, the pore sizes and their accessibility are the critical factors that usually restrict the applicability of the whole system to small substrate molecules. This problem could be partially overcome by applying a co-polymerization approach using an additional ligand in the synthesis of the mesoporous UMCM-1, where a functionalized BDC linker is copolymerized with the ZnO6-cluster and benzene-1,3,5-tribenzoate (BTB). However, because of the topological peculiarity of the framework, all functional groups are located in the micropore, which hinders the interaction with large substrate molecules.

H3BTB is probably one of the most widely used trigonal ligands in MOF chemistry. The CSD substructure search using the BTB fragment results in 411 crystal structures, containing BTB in pure or substituted form [21]. This could be explained by a variety of possible topologies involving bimidol nets containing a trigonal node [22]. Usually, MOFs comprising the BTB ligand have large pores sizes, high pore volumes, and highly accessible pore systems. These features render MOFs with functionalized BTB ligands especially interesting for catalytic and separation applications, wherein the size of the substrate molecules plays a crucial role.

Up to now, investigations on isoreticular synthesis of MOFs with functionalized BTB linkers are limited. This is probably due to the required effort in organic synthesis as functionalized BTB linkers require multiple step synthetic protocols. In the group of Cohen, BTB derivatives with methoxy and hydroxyl groups in one of the ortho positions to the carboxylate donor groups were tested for isoreticular MOF-177 synthesis. While an analog was obtained with methoxy substituted BTB, the hydroxyl substituents lead to a compound with a different topology [23]. Our group reported Zn-based MOFs synthesized with BTB linkers derivatized with chiral auxiliaries [24] at the same position. Depending on the auxiliary and metal used, frameworks with different network topologies were obtained [25]. Zhang and co-workers reported the synthesis of Cd(II) MOFs with H3BTB and 4,4’-bipyridine as ligands. The system’s tolerance to functional groups was studied using modified BTB linker versions with a hydroxyl or amino group attached to the central phenyl ring. As a result, an isoreticular compound was formed with the hydroxylated version of the linker, while the amino functionalization resulted in a framework with a different topology [26]. Interestingly, utilization of aniline-2,4,6-tribenzoate (ATB), which is the BTB linker with one amino substituents in the central phenyl ring, in the synthesis of MOF-177 results in the isoreticular structure [27]. R. Schmidt and co-workers conducted theoretical investigations suggesting that bromine substitution of the two ortho positions in BTB should lead to an alteration of the network topology for the corresponding Cu-based paddle-wheel containing MOFs [13].

In this work, we have studied the structural tolerance of selected BTB-containing MOFs (Table 1) by the introduction of different substituents in the ortho position to the carboxylic group. Eight highly porous MOF materials with open, non-interpenetrated frameworks and high pore volumes were selected for investigations (Table 1). Three different BTB substituted ligands (Fig. 1) were used in this screening: 1) NH2-BTB was chosen having further postsynthetic modification in mind; 2) NHBoc-BTB was used in order to compare the influence of protected and unprotected amino groups on the formation of the desired MOF. Moreover, the Boc group could be easily removed by thermal treatment to form the amino group for postsynthetic modification; 3) mand-BTB was used to study the structural tolerance towards a bulky substituent in the ortho position to the carboxylate groups that could provide spacial proximity to the metal node, which can be beneficial for catalytic applications.

2. Experimental

2.1. Materials and methods

Metal salts, co-ligands (terephthalic acid, 4,4’-bipyridine) and solvents for MOF synthesis, were obtained from commercial vendors and used as received. H4BenzTB was synthesized according to the previously published procedure [28]. H3BTB was synthesized according to the known literature procedures [29,30]. The synthesis details for the linker molecules 3,3’-diaminomio-5’-(3-ammonio-4-carboxylatophenyl)-[11’:3’:1’]-terphenyl-4,4’-dicarboxylate (H3(NH2-BTBC)), 3,3’-bis(tert-butoxycarbonyl)amino)-5’-(3-[[tert-butoxycarbonyl]amino]-4-carboxyphenyl)-[11’:3’:1’]-terphenyl-4,4’-dicarboxylic acid (H3(NH2-BTB)) and 3,3’-bis(S)-2-acetoxy-2-phenylacetamido)-4-carboxyphenyl)-[11’:3’:1’]-terphenyl-4,4’-dicarboxylic acid (H3mand-BTB) are given in Supplementary data S1.

Powder X-ray diffraction measurements were carried out on a STADI P diffractometer (STOE) with Cu-Kα1 radiation (λ = 1.5405 Å) at room temperature. Thermogravimetric analysis was carried out on an STA 409 (Netzsch) with synthetic air as carrier gas with a flow of 100 mL min-1 and a heating rate of 5 K min-1. Nitrogen physisorption measurements were conducted on a BELSORP Max (BEL, Japan) at 77 K up to 1 bar. GC/MS measurements were carried out on a GCMS QP5000 (Shimadzu) equipped with a non-polar BPX5 column (SGE).1H NMR spectroscopy of dissolved MOFs was carried out on an AC 300-P (Bruker).

2.2. Single crystal X-ray diffraction

Single crystals of Cu2(H2O)2[H(NHBoc-BTB)]2 and Cu3(H2O)(NH2-BTB)2(bipy) were transferred in a glass capillary (0.3 mm) with a small amount of solvent. The capillaries were sealed with melted wax. The datasets were collected at BESSY on an AC 300-P (Bruker).

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Table 1
Selected MOF materials for investigation of the structural tolerance.

<table>
<thead>
<tr>
<th>Common name, Composition, Crystal structure</th>
<th>Pore volume (cm³ g⁻¹), Max pore size (Å), Pore limiting diameter (Å)</th>
<th>Co-ligand</th>
<th>Topology</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOF-177, Zn₂O(BTB)₂</td>
<td>2.0, 10.7, 8.8</td>
<td>–</td>
<td>qom</td>
<td>[33]</td>
</tr>
<tr>
<td>UMC-M-1, Zn₂O(BTB)₆(BDC)</td>
<td>2.2, 17.4, 15.4</td>
<td>H₂BDC</td>
<td>muo</td>
<td>[34]</td>
</tr>
<tr>
<td>DUT-6, Zn₂O(BTB)₆(NDC)</td>
<td>2.2, 22.0, 7.7</td>
<td>H₂NDC</td>
<td>ith-d</td>
<td>[29]</td>
</tr>
<tr>
<td>DUT-25, Zn₂O(BTB)₁₀(BenzTB)</td>
<td>2.0, 19.3, 7.1</td>
<td>H₄BenzTB</td>
<td>nbo-b</td>
<td>[37]</td>
</tr>
<tr>
<td>DUT-23(Cu/Zn), M₂(BTB)₄(bipy)</td>
<td>2.0, 19.8, 6.9</td>
<td>4,4'-Bipy</td>
<td>ith-d</td>
<td>[36]</td>
</tr>
<tr>
<td>DUT-34, Cu₆(BTB)₂</td>
<td>2.4, 19.1, 7.0</td>
<td>–</td>
<td>pto</td>
<td>[36]</td>
</tr>
</tbody>
</table>

(continued on next page)
only nitrogen atoms in the ortho-positions to the carboxylate groups in BTB could be localized unambiguously. The lattice solvent molecules could not be localized because of the disorder in the high symmetry space group. The SQUEEZE routine was not applied to the collected data. CCDC-1034130 and CCDC-1034131 contain the supplementary crystallographic data for Cu$_3$(H(NHBoc-BTB))$_2$(H$_2$O)$_4$(DMF)$_4$ and Cu$_3$(NHBoc-BTB)$_2$(bipy). This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.3. MOF synthesis screening

The synthesis screening with BTB derivatives was conducted according to synthetic procedures previously published for MOFs with non-substituted BTB as ligand. Some of the syntheses were downscaled. All of the downscaled syntheses were previously tested with unmodified H$_3$BTB to confirm feasibility. MOF syntheses were run in capped glass Pyrex tubes (10 × 120 mm).

As a general strategy for the screening, the synthetic conditions published for the synthesis of the unmodified MOFs were adopted. Optimization of synthetic conditions followed up, when the product resulting from a screening trial had the potential for further improvement.

Synthesis trials analog to MOF-177 were conducted according to the procedure published in Ref. [34]. Synthesis trials of UMCM-1 analog were conducted according to the procedure published in Ref. [35], but downscaled to one sixth of the original batch size. Synthesis trials analog to DUT-6 were conducted according to the procedure published in Ref. [36], but downscaled to one half of the original batch size. Synthesis trials analog to DUT-

![Linker molecules used for MOF synthesis](image)

**Table 1 (continued)**

<table>
<thead>
<tr>
<th>Common name, Composition, Crystal structure</th>
<th>Pore volume (cm$^3$ g$^{-1}$), Max pore size (Å), Pore limiting diameter (Å)</th>
<th>Co-ligand</th>
<th>Topology</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>DUT-9, Ni$_6$O$_2$(BTB)$_2$</td>
<td>2.4, 22.6, 14.4</td>
<td>–</td>
<td>eea</td>
<td>[35]</td>
</tr>
</tbody>
</table>

Fig. 1. Linker molecules used for MOF synthesis: H$_3$BTB (a), H$_3$(NH$_2$-BTB) (b), H$_3$(NHBoc-BTB) (c) and H$_3$(mand-BTB) (d).
23(Cu), DUT-23(Zn) and DUT-34 were conducted according to the published procedure [38], but downscaled to one half, one quarter and one fifth of the original batch size, respectively. Synthesis trials analog to DUT-25 were conducted according to the procedure published in Ref. [39]. For synthesis of mand-DUT-25, the reaction was scaled up to 150% of the original batch size and reaction time was prolonged to 120 h.

3. Results and discussion

For the crystallization of amino-functionalized highly porous MOFs as starting materials for variable postsynthetic functionalizations, H₃(NH₂-BTB) bearing three amino groups (Fig. 1) was synthesized. Unfortunately, synthesis screening applying H₃(NH₂-BTB) in the established synthesis procedures for the targeted MOFs tabulated in Table 1, resulted in amorphous reaction products in most of the cases. Only in the case of DUT-6, a few single crystals could be found in the reaction product and the structure could be confirmed by single X-ray diffraction analysis. However, the bulk of the reaction product was amorphous. All attempts to optimize the synthesis conditions by varying reaction parameters such as the type of Zn²⁺-source or adding modulators such as acetic acid or benzoic acid to the reaction mixture did not afford highly crystalline and phase pure products. Similar optimization of synthetic conditions was attempted for MOF-177 analog as well, including utilization of basic zinc acetate as Zn source (following controlled SBU approach). Those experiments have also resulted in amorphous reaction products. It has to be noted that Telfer et al. reported similar problems while applying amino substituted 4,4'-biphenyl dicarboxylic acid (H₂(NH₂-BPDC)) in an IRMOF synthesis [19].

In the case of the targeted copper containing analogs of DUT-23 and DUT-34 (Table 1), utilization of NH₂-BTB leads to a rapid precipitation of amorphous material. Modification of the reaction conditions, such as addition of different acids as modulator or variation of the solvent mixture did not improve the crystallinity of the products. This observation could point to an undesired interaction between the copper ions and the amino groups.

According to the ¹H NMR spectrum of H₃(NH₂-BTB) in DMSO-d₆, the solvated linker exists as a zwitterion: the carboxylic acid functions are deprotonated while the amino functions are protonated. It should be mentioned that typically, the acid functions are gradually deprotonated in the course of the solvothermal reaction. This gradual deprotonation allows the crystallization process to proceed at a rate that allows for healing of defects [40]. If the linker involved in the reaction is present in its fully deprotonated state, the reaction rate may be very high, preventing healing of defects and resulting in amorphous reaction products. According to Telfer et al., for a successful synthesis of the amino functionalized IRMOF structure, the amino functionality can be protected with a Boc protecting group. Therefore, the Boc protected amino-BTB linker (H₃(NHBoc-BTB)) was synthesized and utilized in further synthetic attempts.
The protection of the amino group was performed starting with the ester form of the amino functionalized BTB derivative. Direct single protection of the amino groups was not possible synthetically. Therefore, two Boc protecting groups were first introduced per amino group and afterward one of these groups was removed selectively, using the method developed by Martin et al. [41] (for more details see Supplementary data S1).

Unfortunately, the utilization of \( \text{H}_3\text{NHBoc-BTB} \) in combination with the \( \text{Zn}_4\text{O}_6^{4-} \) cluster again did not lead to the formation of crystalline products. Only in the case of copolymerization with \( \text{H}_4\text{BenzTB} \), the isoreticular analog of DUT-25 could be obtained as isolated single crystals (The isostructurality was verified by determining the corresponding cell parameters by single crystal X-ray diffraction.). However, the powder XRD pattern indicates the predominant formation of amorphous reaction product (Fig. S3).

Using copper nitrate as metal source for the SBU under reaction conditions typical for DUT-23(Cu) and DUT-34, crystalline products could be obtained. However, single crystal X-ray diffraction study reveals the formation of topologically different frameworks in both cases.

If the reaction conditions for DUT-34 were applied, a coordination network crystallizing in the monoclinic space group \( P2_1/n \) is formed (Table 2). The asymmetric unit contains one copper atom, one monoprotonated NHBoc-BTB linker molecule, two water and two DMF (DMF – \( \text{N,N-dimethylformamide} \)) molecules. The overall composition of the compound is \( \text{Cu}_3(\text{H}_2\text{O})_2(\text{H}\text{NHBoc-BTB})_2(\text{bipy}) \龠 2\text{H}_2\text{O} \cdot 4\text{DMF} \) (1). The structure is based on Cu paddle-wheel units interconnected by only two carboxylic groups from the NHBoc-BTB ligand resulting in a two dimensional 4\( ^4 \text{-sq} \) net (Fig. 2).

The third carboxylic group of NHBoc-BTB remains protonated and does not contribute to the network connectivity, but forms hydrogen bonds with the lattice DMF molecules (Table S2). The resulting layers run parallel to the (101) plane.

The analysis of crystallographic porosity, performed using PLATON software [42], shows no accessible void in the crystal structure.

If synthetic conditions of DUT-23(Cu) were applied for the synthesis using \( \text{H}_3\text{NHBoc-BTB} \) instead of \( \text{H}_2\text{BTB} \), a product, which crystallizes in the tetragonal space group \( I4_1/amd \) with the framework composition \( \text{Cu}_3(\text{H}_2\text{O})_2(\text{H}\text{NHBoc-BTB})_2(\text{bipy}) \) (DUT-109) is formed (Table 2). The asymmetric unit contains two Cu\(^{2+} \) atoms, located in the 16\( h \) (\( \text{mm} \)) and 8\( e \) (\( \text{mm} \)) positions of the unit cell which belong to the different, symmetrically independent paddle-wheel units. These are interconnected by NHBoc-BTB linkers into the 3D framework. Remarkably, symmetry dependent paddle-wheel clusters involving Cu atoms in 16\( h \) positions are additionally interconnected by 4,4’-bipyridine ligands in axial direction, increasing the connectivity of the node from 4 (square-planar node) to 6 (octahedral node). The interconnection of the paddle-wheels along [100] and [010] directions should considerably improve the robustness of the framework. At the same time, paddle-wheels involving 8\( e \) Cu atoms are coordinated by terminal water/DMF ligands and therefore, remain square planar nodes. The simplification of the crystal structure leads to the 3-nodal 3,4,6-connected network. Although this network could not be classified by TOPOS, it can be considered as a cross linked iab topology [22] (also sqc5580 net [38]) with interconnected 8\( d \) vertices (Fig. 3). The possibility of the formation of this type of framework involving paddle-wheel as cluster and trigonal ligand, where only 75% of the paddle wheels are connected by a linear cross-linker, was discussed earlier by us [38] and DUT-109 is the first example of such MOF achieved synthetically.

The structure contains channels running along the crystallographic \( a \)- and \( b \)-directions measuring 12 Å in diameter. The pore limiting diameter is 6.5 Å. The pore volume of the desolvated framework calculated theoretically using the Poreblazer 3.0 software [43] is 0.93 cm\(^3\) g\(^{-1}\).

The analysis of \( ^1\text{H} \) NMR spectra of dissolved material revealed the preservation of the Boc-protecting groups during synthesis. Unfortunately, none of the attempts to activate the compound for gas physisorption measurements were successful. Neither applying dynamic vacuum to the ethanol exchanged sample nor supercritical \( \text{CO}_2 \) activation could remove the solvent molecules from the pores without framework collapse. In each case, an amorphous, non porous compound was obtained after activation.

Therefore, liquid phase adsorption of ethyl cinnamate from \( \text{n-heptane at } 25^\circ\text{C} \) was performed in order to verify the framework’s porosity and accessibility. The uptake was compared with other MOFs, which were also measured using the method described by Henschel et al. [44]. DUT-109 adsorbs 514 mg g\(^{-1}\) of ethyl cinnamate, clearly demonstrating the framework accessibility in liquid phase. Furthermore, the uptake of ethyl cinnamate with respect to the pore volume is significantly larger compared to compounds without open metal sites or polar side groups (Fig. 4). In our view, this result is in good accordance with the presence of accessible Cu-paddlewheels not coordinated by 4,4’-bipyridine as well as the polar NHBoc-substituents.
In order to make the substituents of DUT-109 susceptible to post-synthetic modifications, the amino function should be deprotected. In general, the Boc protecting group can be removed thermally or by acid treatment. Acid treatment could not be applied in this particular case because of the instability of the compound against acids. Telfer et al. succeeded in deprotecting the modified IRMOF-9 by heating activated samples [19] up to 150 °C. Due to the framework flexibility and as a consequence the framework collapse during activation, this procedure could not be applied for DUT-109. Therefore, the deprotection experiments were carried out using DUT-109 suspended in DMF or mesitylene. The suspension was heated for 24 h to 130 °C or 150 °C, respectively. The thermally treated samples were characterized by PXRD (Fig. S2 Supplementary data) and 1H NMR to monitor the crystallinity and the chemical composition of the linker. It was found, that by heating to 130 °C only partial deprotection could be achieved in both solvents used. Heating to 150 °C causes deprotection of ca. 90% of the linker molecules, but is accompanied by a significant loss in crystallinity of the samples. This loss of crystallinity is more pronounced for the samples treated in DMF.

Since starting MOF materials for post synthetic functionalization could not be synthesized in good yield and under full preservation of crystallinity, the pre-synthetic functionalization route was also applied to selected structures as well. Starting from H3(NH2-BTB), H3(mand-BTB) could be synthesized by one synthetic step (for synthesis details see Supplementary data). With this linker, the structural analog to DUT-25 (mand-DUT-25) could be obtained according to powder X-ray diffraction measurements (Fig. 5, Fig. S4, Table S1). The presence of the side groups in the mand-DUT-25 was proven by 1H NMR after mild

**Table 2**

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>Cu2(H(NHBoc-BTB))2(H2O)4(DMF)4 (1)</th>
<th>Cu3(H2O)(NHBoc-BTB)2(bipy) (DUT-109)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight, g/mol</td>
<td>Cu2H14Cu2N2O32</td>
<td>Cu3H9Cu3N8O13</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, P21</td>
<td>Tetragonal, I41/amd</td>
</tr>
<tr>
<td>Unit cell dimensions, Å, deg.</td>
<td>a = 9.6800(19)</td>
<td>a = 27.860(4)</td>
</tr>
<tr>
<td></td>
<td>b = 24.270(5)</td>
<td>c = 53.540(11)</td>
</tr>
<tr>
<td></td>
<td>c = 23.410(5)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>β = 90.07(3)</td>
<td></td>
</tr>
<tr>
<td>Volume, Å³</td>
<td>5500(2)</td>
<td>41557(14)</td>
</tr>
<tr>
<td>Z, Calc. density, g/cm³</td>
<td>2, 1.236</td>
<td>8, 0.419</td>
</tr>
<tr>
<td>F(000)</td>
<td>2148</td>
<td>3438</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>−11 ≤ h ≤ 8</td>
<td>−31 ≤ h ≤ 33</td>
</tr>
<tr>
<td></td>
<td>−29 ≤ k ≤ 29</td>
<td>−33 ≤ k ≤ 21</td>
</tr>
<tr>
<td></td>
<td>−20 ≤ l ≤ 28</td>
<td>−63 ≤ l ≤ 59</td>
</tr>
<tr>
<td>Reflections collected/unique</td>
<td>23,111/9274 (Rint = 0.0176)</td>
<td>62,742/9523 (Rint = 0.0515)</td>
</tr>
<tr>
<td>Data/parameters</td>
<td>9274/656</td>
<td>62742/133</td>
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<tr>
<td>GoF on F²</td>
<td>1.080</td>
<td>1.598</td>
</tr>
<tr>
<td>R [I &gt; 2σ(I)]</td>
<td>0.0503</td>
<td>0.1186</td>
</tr>
<tr>
<td>wR (all data)</td>
<td>0.1440</td>
<td>0.3927</td>
</tr>
<tr>
<td>Largest diff. peak/hole, e/Å³</td>
<td>0.480/0.474</td>
<td>0.168/0.302</td>
</tr>
</tbody>
</table>

* R₁ = Σ||Fo| − |Fc||/Σ|Fo|; wR = Σw(Fo² − Fc²)²/Σw(Fo²)².1/2.

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decomposition of the supercritically dried sample in DMSO and deuterium chloride (Fig. S5).

To desolvate mand-DUT-25 for adsorption experiments, supercritical CO2 drying was applied. Nitrogen physisorption at 77 K showed a saturation uptake of 100 cm3 g−1 resulting in a specific pore volume of 0.16 cm3 g−1. The BET surface area is 400 m2 g−1 (Fig. 6). However, simulation of the crystal structure of mand-DUT-25 using Materials Studio by Accelrys with further calculation of the textural properties using Poreblazer software [43], results in a much higher value for the expected pore volume of 1.23 cm3 g−1 and geometrically calculated accessible surface area of ca. 3300 m2 g−1. The presence of the bulky substituents hence seems to prevent complete and nondestructive framework desolvation in this case. All trials to synthesize the remaining targeted MOFs, such as DUT-23/34, DUT-6, DUT-9 or MOF-177 analogs failed.

The overall results of the MOF synthesis screening are summarized in Table 3. Most of the substituted BTB derivatives show a rather limited compatibility with the original BTB-containing MOF systems, providing valuable information concerning the future design of functionalized MOFs. While the formation of the SBU can be considered as a critical step in MOF synthesis [40], the results of this work once again clearly demonstrate the crucial role of substituents in ligand molecules and their effect on the formation of selected framework topologies, particularly in the case of Cu-paddlewheel based MOFs DUT-23(Cu) and DUT-34. Interestingly, while four different ZnO-based MOFs were screened for compatibility with the BTB derivatives, successful synthesis of structural analogs was observed in the case of DUT-25 only. This possibly points to the fact that the framework of DUT-25 (nbo-b topology) is much more tolerant towards sterically demanding substituents than other investigated frameworks, involving the ZnO SBU as a node.

### 4. Conclusions

Three new derivatives of H3BTB, namely – H3(NH2-BTB), H3(NHBoc-BTB) and H3(mand-BTB) were used in the crystallization of eight selected BTB containing highly porous non-interpenetrated MOFs. In summary, five frameworks, namely NH2-DUT-6, NHBoc-DUT-25, mand-DUT-25, Cu2(H2O)2(H(NHBoc-BTB))2 (I) and Cu2(H2O)(NHBOc-BTB)2(bipy) (DUT-109) could be identified. NH2-DUT-6 and NHBoc-DUT-25 could not be synthesized as pure phase.

### Table 3

<table>
<thead>
<tr>
<th>MOF</th>
<th>NH2-BTB</th>
<th>NHBoc-BTB</th>
<th>mand-BTB</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOF-177</td>
<td>×</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UMCM-1</td>
<td>×</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DUT-6</td>
<td>NH2-DUT-6a</td>
<td>×</td>
<td></td>
</tr>
<tr>
<td>DUT-25</td>
<td>×</td>
<td>NHBoc-DUT-25a</td>
<td></td>
</tr>
<tr>
<td>DUT-23(Zn)</td>
<td>×</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DUT-23(Cu)</td>
<td>×</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DUT-34</td>
<td>×</td>
<td>New structure: Cu2(H2O)(NHBOc-BTB)2(bipy) (DUT-109)</td>
<td>×</td>
</tr>
<tr>
<td>DUT-9</td>
<td>×</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Phase purity could not be achieved.*

400 m2 g−1 and a specific pore volume of 0.16 cm3 g−1. While the porosity of DUT-109, synthesized using established DUT-23(Cu) synthesis procedure, could not be investigated by gas physisorption, a high adsorption capacity of 514 mg g−1 in liquid phase adsorption of ethyl cineammate in n-heptane was achieved. Thermal deprotection of the amino groups was possible at 150 °C in DMF or mesitylene, but coincided with some loss of crystallinity.

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### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.micromeso.2015.02.055.
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