

Cite this: *Chem. Commun.*, 2012, **48**, 11196–11198

www.rsc.org/chemcomm

## COMMUNICATION

Amino substituted  $\text{Cu}_3(\text{btc})_2$ : a new metal–organic framework with a versatile functionality†

Katharina Peikert, Frank Hoffmann and Michael Fröba\*

Received 27th August 2012, Accepted 27th September 2012

DOI: 10.1039/c2cc36220a

**A new amino substituted tricarboxylate linker and the new metal–organic framework  $\text{Cu}_3(\text{NH}_2\text{btc})_2$  have been synthesised. The new MOF shows good adsorption properties and is suitable for postsynthetic modification to form an amide functionalised framework.**

Metal–Organic Frameworks (MOFs) are crystalline, inorganic–organic hybrid materials, which are characterised by their porosity and the associated high specific surface areas.<sup>1</sup> MOF structures can be tailored quite easily by combining different metal ions or metal–oxygen clusters and organic ligands of different size and shape. This results in a variety of properties, such as tuneable pore sizes,<sup>2</sup> large inner pore volumes and specific chemical properties of the pore walls.<sup>3</sup> MOFs can also be designed to contain “open” metal centres, which exhibit high affinities towards certain gases. These properties turn MOFs into prime candidates for use as gas storage and separation materials.<sup>4</sup>

The classical way to incorporate functional groups into a MOF is the modification of the organic ligand with specific substituents before synthesising the MOF itself. This approach has resulted in MOFs with functional groups such as  $-\text{Br}$ ,  $-\text{NH}_2$ ,  $-\text{CH}_3$ ,  $-\text{OH}$ ,  $-\text{OC}_3\text{H}_7$ , and  $-\text{C}_2\text{H}_4$ , known for example from the IRMOF<sup>2</sup> or MIL<sup>5</sup> series. Another route for obtaining functionalised MOFs is the postsynthetic modification (PSM). Since the first detailed studies in 2007 by Wang and Cohen<sup>6</sup> this route is a growing and promising approach in the area of MOF chemistry. One of the advantages of this synthetic methodology is the possibility to create functional groups inside the MOF which are not stable under the solvothermal conditions in which the majority of MOFs are synthesised usually. Furthermore, it is possible to prepare topologically identical, but functionally different frameworks.<sup>7</sup> PSM studies show that this approach can lead to improved gas adsorption<sup>8</sup> and catalytic properties.<sup>9</sup>

$\text{Cu}_3(\text{btc})_2$  (also known as HKUST-1; btc = 1,3,5-benzenetricarboxylate) is one of the first and best-known MOFs. Since its publication<sup>10</sup> by Chui *et al.* in 1999 there have been continuous efforts to improve the synthesis and activation procedure of  $\text{Cu}_3(\text{btc})_2$ . Most studies have focused on gas adsorption properties.<sup>11</sup> Ingleson *et al.* did PSM studies on  $\text{Cu}_3(\text{btc})_2$  by coordinating 4-(methylamino)-pyridine (4-map) to the Cu centres. Thus, they introduced accessible secondary amine functionalities that react with nitric oxide (NO) to form *N*-diazonium diolates (so-called NONOates).<sup>12</sup> Since NO is an extremely important biological signaling molecule, there is great interest in developing NO storage and delivery materials.<sup>13</sup> Besides the storage as NONOate a second central method for storing NO in MOFs is the coordination to “open”, *i.e.* coordinatively unsaturated metal centres.

In spite of the great research interest in  $\text{Cu}_3(\text{btc})_2$ , there is only one report on functionalisation of the btc ligand. Very recently, Cai *et al.* presented two copper frameworks constructed from  $\text{H}_3\text{btc}$  that has been functionalised with methyl and ethyl groups.<sup>14</sup> Although the reaction conditions for the MOF synthesis were the same as those reported for the  $\text{Cu}_3(\text{btc})_2$  synthesis<sup>11a</sup> the resulting frameworks exhibit a different topology.

Herein, we present the synthesis and characterisation of the new amino substituted tricarboxylate linker 2-amino-1,3,5-benzenetricarboxylate ( $\text{NH}_2\text{btc}$ ) as well as the synthesis, structure and properties of the resulting metal–organic framework  $\text{Cu}_3(\text{NH}_2\text{btc})_2$ , which we called UHM-30 (UHM = *University of Hamburg Materials*) (see Fig. 1). The new MOF is isostructural to  $\text{Cu}_3(\text{btc})_2$  and opens a way to a functionalised  $\text{Cu}_3(\text{btc})_2$  series, as we offer amino groups inside the MOF on the one hand and could show the accessibility of these groups by PSM on the other hand. In this regard the amino group exhibits great potential for further modification. In the literature

Department of Chemistry, Institute of Inorganic and Applied Chemistry, University of Hamburg, Martin-Luther-King-Platz 6, 20146 Hamburg, Germany. E-mail: froeba@chemie.uni-hamburg.de; Fax: +49 40 42838 6348; Tel: +49 40 42838 3100

† Electronic supplementary information (ESI) available: Synthetic details, characterisation of all compounds, crystallographic details, and adsorption isotherms. CCDC 896694. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc36220a

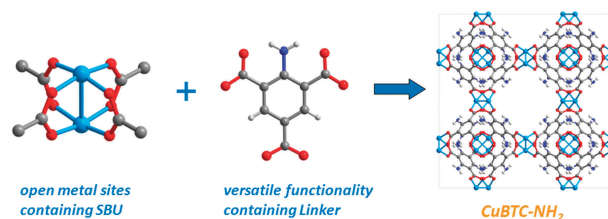


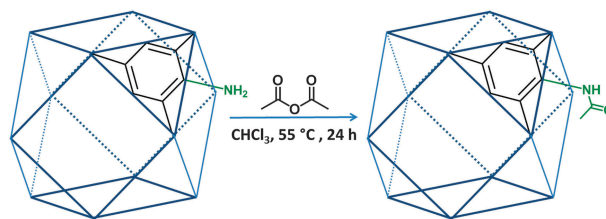
Fig. 1 Visualisation of the construction principle of  $\text{Cu}_3(\text{NH}_2\text{btc})_2$ .

a multitude of modification reactions of primary amino groups in MOFs is reported. A few examples are the incorporation of amides,<sup>15</sup> *N*-diazonium diolates,<sup>16</sup> alcohols<sup>17</sup> and azides.<sup>18</sup> In contrast to the IRMOF and MIL series our structure enables the combination of “open” metal sites and functional groups in one material. In this context it should be possible to store NO in this material *via* chemisorption as NONOate and *via* physisorption at the “open” metal sites. Different release kinetics for the chemisorbed and physisorbed NO species are conceivable.

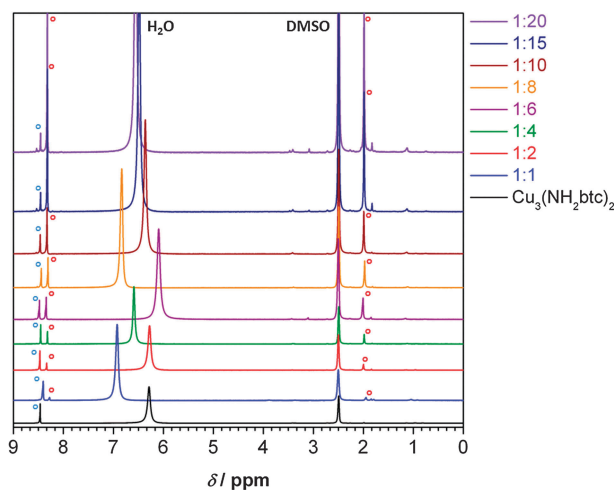
The synthesis of the new linker could be accomplished in a five-step reaction starting with 2-fluoro-1,3,5-trimethylbenzene. Solvothermal reaction of NH<sub>2</sub>btc and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O in dimethylacetamide (DMA)–water (H<sub>2</sub>O) led to greenish crystals of Cu<sub>3</sub>(NH<sub>2</sub>btc)<sub>2</sub> in high yields.<sup>†</sup>

Single X-ray crystal structure analysis reveals that Cu<sub>3</sub>(NH<sub>2</sub>btc)<sub>2</sub> is isostructural to Cu<sub>3</sub>(btc)<sub>2</sub>.<sup>†</sup> According to the three possible orientations of the linker during the incorporation into the framework the amino group shows a positional disorder over three sites, all with a site occupation factor (s.o.f) of 1/3 (for details, see ESI<sup>†</sup>). To remove the solvent used during the synthesis Cu<sub>3</sub>(NH<sub>2</sub>btc)<sub>2</sub> was activated *via* solvent exchange. Complete activation could be ensured by thermogravimetric and differential thermal (TG-DTA) studies coupled with mass spectrometry (Fig. S2, ESI<sup>†</sup>). The N<sub>2</sub> physisorption measurement shows a typical type-I isotherm (Fig. S4, ESI<sup>†</sup>). The analysis of the isotherm reveals a specific surface area of  $S_{\text{BET}} = 1834 \text{ m}^2 \text{ g}^{-1}$  (calculated from the adsorption branch and in the relative pressure interval from 0.001 to 0.025) and a micropore volume of  $V_{\text{pore}} = 0.69 \text{ cm}^3 \text{ g}^{-1}$  ( $d < 2 \text{ nm}$  calculated at  $p/p_0 = 0.18$ ). These values are very similar to the values known for Cu<sub>3</sub>(btc)<sub>2</sub>.<sup>11c</sup> Both low (up to 1 bar) and high pressure (up to 45 bar) volumetric CO<sub>2</sub> and CH<sub>4</sub> adsorption measurements were carried out at 298 K. Under the same pressure conditions H<sub>2</sub> adsorption isotherms were measured at 77 K (Fig. S5 and S6, ESI<sup>†</sup>). The results are summarised in Table 1. The physisorption measurements for Cu<sub>3</sub>(NH<sub>2</sub>btc)<sub>2</sub> show similar adsorption properties to those of Cu<sub>3</sub>(btc)<sub>2</sub>. Whereas the results for CO<sub>2</sub> and CH<sub>4</sub> at 45 bar show slightly lower adsorption capacities, the values at 1 bar are slightly improved compared to those of Cu<sub>3</sub>(btc)<sub>2</sub>.<sup>19</sup>

To prove the accessibility of the amino groups for post-synthetic modification the solvent exchanged MOF was treated with acetic anhydride to build an amide functionality (Fig. 2). A typical reaction was carried out with 77.3 mg MOF in CHCl<sub>3</sub> at 55 °C for 24 h, followed by extensive washing with methanol. The amount of acetic anhydride was varied from 1 equivalent up to 20 equivalents relating to the chemical amount of amino groups. The modification was confirmed by nuclear magnetic resonance (NMR) spectroscopy and electrospray mass spectrometry (ESI-MS). The <sup>1</sup>H NMR



**Fig. 2** Postsynthetic modification of Cu<sub>3</sub>(NH<sub>2</sub>btc)<sub>2</sub> with acetic anhydride.



**Fig. 3** <sup>1</sup>H NMR spectra of digested Cu<sub>3</sub>(NH<sub>2</sub>btc)<sub>2</sub> (black) and modified samples by the use of different amounts of acetic anhydride (coloured). The blue circles mark the unmodified NH<sub>2</sub>btc, the red ones show the modified linker. The signals are normalised to the peak at 8.5 ppm.

spectra of the modified samples show a highfield shift of the aromatic proton signal and a corresponding signal for the acetic methyl group (Fig. 3). By comparing the relative integrated areas of the aromatic resonances between the modified and unmodified linkers the degree of conversion of the amino groups in the framework could be determined. Depending on the concentration of acetic anhydride it is possible to convert up to 92% of the amino groups. The results are summarised in Table 2.

ESI-MS studies gave additional evidence of the modification as the sodium adduct of the amide could be detected (Fig. S7, ESI<sup>†</sup>). As evidenced by accompanied powder XRD measurements (Fig. 4) the degree of crystallinity of the framework decreases with increasing degree of conversion of the amino groups. This observation is in agreement with the results obtained for the BET surface areas of the functionalised MOFs, which are summarised in Table 2. As the measurements show the porosity of the framework is reduced by increasing degree of conversion. The material treated with

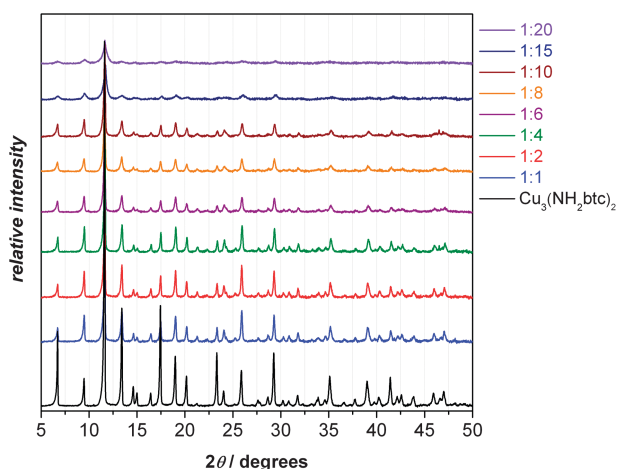
**Table 1** H<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> uptake in Cu<sub>3</sub>(NH<sub>2</sub>btc)<sub>2</sub> at low and high pressures compared to the literature known values of Cu<sub>3</sub>(btc)<sub>2</sub>

Fluid	H <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>
Cu <sub>3</sub> (NH <sub>2</sub> btc) <sub>2</sub> uptake 1 bar	2.28 wt%	1.04 mmol g <sup>-1</sup>	5.26 mmol g <sup>-1</sup>
Max. uptake	3.35 wt% (21 bar)	8.66 mmol g <sup>-1</sup> (43 bar)	11.7 mmol g <sup>-1</sup> (23 bar)
Cu <sub>3</sub> (btc) <sub>2</sub> uptake 1 bar	2.27 wt% <sup>19a</sup>	0.98 mmol g <sup>-1</sup> (295 K) <sup>19b</sup>	4.69 mmol g <sup>-1</sup> (295 K) <sup>19b</sup>
Max. uptake	3.53 wt% (22 bar) <sup>19c</sup>	— <sup>19d</sup>	15.8 mmol g <sup>-1</sup> (22 bar) <sup>19e</sup>

**Table 2** Conversion degree of  $\text{Cu}_3(\text{NH}_2\text{btc})_2$  to  $\text{Cu}_3(\text{NHCOCH}_3\text{btc})_2$  depending on the acetic anhydride ( $\text{Ac}_2\text{O}$ ) concentration and the resulting BET surface areas of  $\text{Cu}_3(\text{NHCOCH}_3\text{btc})_2$

$\text{NH}_2 : \text{Ac}_2\text{O}$	Conversion <sup>a</sup> (%)	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )
1 : 1	14	1149
1 : 2	26	1137
1 : 4	42	1124
1 : 6	55	943
1 : 8	66	481
1 : 10	73	640
1 : 15	87	—
1 : 20	92	—

<sup>a</sup> The percent conversion values are the arithmetic average of three independent experiments.



**Fig. 4** Powder X-ray diffractograms of  $\text{Cu}_3(\text{NH}_2\text{btc})_2$  (black) and the modified samples (coloured).

15 or 20 equivalents of acetic anhydride even loses its porosity completely. This leads to the assumption that the framework is destroyed by the treatment with higher amounts of acetic anhydride than 10 equivalents. This result is not very surprising, since acetic acid is built during the PSM reaction and  $\text{Cu}_3(\text{btc})_2$  is known to be not stable in acid media. However, it is possible to get materials with a tuneable degree of conversion up to 70%, which still show an acceptable porosity. The thermal stability of the modified samples slightly increases relative to the unmodified  $\text{Cu}_3(\text{NH}_2\text{btc})_2$  (Fig. S8, ESI†).

In summary, we have successfully synthesised a new tricarboxylic linker and the resulting amino substituted MOF  $\text{Cu}_3(\text{NH}_2\text{btc})_2$ . The MOF shows good adsorption properties for a series of gases. The accessibility of the amino groups could be successfully proved by postsynthetic modification with acetic anhydride. The amount of acetic anhydride was varied from 1 equivalent up to 20 equivalents relating to the amount of amino groups. The modification was verified by  $^1\text{H}$  NMR and ESI-MS analysis. XRD and  $\text{N}_2$  physisorption studies showed the breakup of the framework by the use of acetic anhydride concentrations higher than 10 equivalents. However, it was possible to get porous materials with a tuneable degree of conversion up to 70%. The combination of “open” metal sites and accessible amino functionalities in this new MOF reveals great potential for use as NO storage material, as it should be possible to store NO *via* chemisorption

as NONOate and *via* physisorption at the “open” metal sites. The preparations for NO adsorption, storage and release experiments are in process.

This work was supported by the Deutsche Forschungsgemeinschaft (DFG: Fr 1372/18-2) as part of the priority program 1362 (Porous metal–organic frameworks). We thank Matthias Rogaczewski for support in the laboratory.

## Notes and references

- (a) G. Férey, *Chem. Soc. Rev.*, 2008, **37**, 191; (b) S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; (c) J. L. C. Rowsell and O. M. Yaghi, *Microporous Mesoporous Mater.*, 2004, **73**, 3.
- M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O’Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469.
- K. K. Tanabe and S. M. Cohen, *Chem. Soc. Rev.*, 2011, **40**, 498.
- (a) R. E. Morris and P. S. Wheatley, *Angew. Chem., Int. Ed.*, 2008, **47**, 4966; (b) J.-R. Li, R. J. Kupper and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477.
- S. Biswas, T. Ahnfeldt and N. Stock, *Inorg. Chem.*, 2011, **50**, 9518.
- Z. Wang and S. M. Cohen, *J. Am. Chem. Soc.*, 2007, **129**, 12368.
- (a) Z. Wang and S. M. Cohen, *Chem. Soc. Rev.*, 2009, **38**, 1315; (b) K. K. Tanabe and S. M. Cohen, *Chem. Soc. Rev.*, 2011, **40**, 498.
- (a) K. L. Mulfort, O. K. Farha, C. L. Stern, A. A. Sarjeant and J. T. Hupp, *J. Am. Chem. Soc.*, 2009, **131**, 3866; (b) Z. Wang, K. K. Tanabe and S. M. Cohen, *Chem.–Eur. J.*, 2010, **16**, 212; (c) Y.-S. Bae, O. K. Farha, J. T. Hupp and R. Q. Snurr, *J. Mater. Chem.*, 2009, **19**, 2131.
- (a) K. K. Tanabe and S. M. Cohen, *Angew. Chem., Int. Ed.*, 2009, **48**, 7424; (b) X. Zhang, F. X. Llabrés I Xamena and A. Corma, *J. Catal.*, 2009, **265**, 155; (c) A. Corma, M. Iglesias, F. X. Llabrés I Xamena and F. Sánchez, *Chem.–Eur. J.*, 2010, **16**, 9789.
- S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148.
- (a) K. Schlichte, T. Kratzke and S. Kaskel, *Microporous Mesoporous Mater.*, 2004, **73**, 81; (b) P. Krawiec, M. Kramer, M. Sabo, R. Kunschke, H. Fröde and S. Kaskel, *Adv. Eng. Mater.*, 2006, **8**, 293; (c) J. Liu, J. T. Culp, S. Natesakhawat, B. C. Bockrath, B. Zande, S. G. Sankar, G. Garberoglio and J. K. Johnson, *J. Phys. Chem. C*, 2007, **111**, 9305; (d) J. L. C. Rowsell and O. M. Yaghi, *J. Am. Chem. Soc.*, 2006, **128**, 1304.
- M. J. Ingleson, R. Heck, J. A. Gould and M. J. Rosseinsky, *Inorg. Chem.*, 2009, **48**(21), 9986.
- (a) A. C. McKinlay, R. E. Morris, P. Horcajada, G. Gèrey, P. Couvreur and C. Serre, *Angew. Chem., Int. Ed.*, 2010, **49**, 6260; (b) A. C. McKinlay, B. Xio, D. S. Wragg, P. S. Wheatley, I. L. Megson and R. E. Morris, *J. Am. Chem. Soc.*, 2008, **130**, 10440; (c) B. Xiao, P. S. Wheatley, X. 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.
- Y. Cai, Y. Zhang, Y. Huang, S. R. Marder and K. S. Walton, *Cryst. Growth Des.*, 2012, **12**(7), 3709.
- A. J. Garibay and S. M. Cohen, *Chem. Commun.*, 2010, **46**, 7700–7702.
- J. G. Nguyen, K. K. Tanabe and S. M. Cohen, *CrystEngComm*, 2010, **12**, 2335.
- W. Morris, C. J. Doonan and O. M. Yaghi, *Inorg. Chem.*, 2011, **50**(15), 6853.
- M. Savonnet, D. Bazer-Bachi, N. Bats, J. Perez-Pellitero, E. Jeanneau, V. Lecocq, C. Pinel and D. Farrusseng, *J. Am. Chem. Soc.*, 2010, **132**, 4518.
- (a) B. Xiao, P. S. Wheatley, X. B. Zhao, A. J. Fletcher, S. Fox, A. G. Rossi, S. Megson, S. Bordiga, L. Regli, K. M. Thomas and R. E. Morris, *J. Am. Chem. Soc.*, 2007, **129**, 1203; (b) Q. M. Wang, D. M. Shen, M. Bulow, M. L. Lau, S. G. Deng, F. R. Fitch, N. O. Lemcoff and J. Semancin, *Microporous Mesoporous Mater.*, 2002, **55**, 217; (c) B. Panella, M. Hirscher, H. Pütter and U. Müller, *Adv. Funct. Mater.*, 2006, **16**, 520; (d) To the best of our knowledge no experimental high pressure measurements of  $\text{CH}_4$  on  $\text{Cu}_3(\text{btc})_2$  have been reported so far; (e) J. R. Karra and K. S. Walton, *J. Phys. Chem. C*, 2010, **114**, 15735.