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ARTICLE

Synthesis, functionalisation and post-synthetic modification of bismuth metal-organic frameworks

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Two new bismuth metal-organic frameworks (Bi-MOFs) have been discovered using high throughput experiments employing bismuth(III) nitrate pentahydrate and triazine-2,4,6-triyl-trisbenzoic acid (H_3TATB). Long reaction times (~ 5 d) in a water/DMF-mixture resulted in the formation of $[Bi_2(O)(OH)(TATB)]\cdot H_2O$ (denoted as CAU-35). By switching to short reaction times and a methanol/DMF-mixture as the solvent, an analogue of CAU-7-BTB with the composition $[Bi(TATB)]\cdot DMF\cdot 6H_2O$ (denoted as CAU-7-TATB) was obtained. The use of the amino-functionalised H_3TATB linker (H_3TATB-NH_2) resulted in the formation of a functionalised porous Bi-MOF with the composition $[Bi(TATB\text{-}NH_2)]\cdot 5H_2O\cdot 0.5DMF$ (CAU-7-TATB-NH_2). The structures of CAU-35 and CAU-7-TATB were successfully solved and refined from PXRD data. CAU-7-TATB-NH_2 was post-synthetically modified using anhydrides (acetic anhydride, valeric anhydride), cyclic anhydrides (succinic anhydride, phthalic anhydride) and 1,3-propane sultone. The degree of conversion ranges from 33 % to 79 %.

Introduction

Tuneable properties and high specific surface areas made metal-organic frameworks (MOFs) one of the main focussed compounds in chemistry over the last decade.[1] Many different metal ions have been incorporated into MOF structures, but for future applications most often abundant and non-toxic metal ions are the elements of choice.[2] Bismuth compounds are generally known to be non-toxic, even though bismuth is the heaviest stable element in nature.[3] So far, only three Bi-MOFs have been published which possess permanent porosity, i.e. CAU-7,[4] NOTT-220[5] and CAU-17[6]. Among these, CAU-7-BTB ([Bi(BTB)], BTB^{3-} = 1,3,5-benzenetrisbenzoate, Scheme 1) has been proven to be catalytically active in the hydroxymethylation of furane derivatives.[4] In addition, Bi-MOFs have also been studied for application in gas storage,[5] photocatalysis[7] and photoluminescence.[8]

The introduction of functional groups into the MOF scaffold is a common way to adjust their chemical and physical properties and thereby extend their possible field of applications. This can be achieved either by directly using a functionalised linker in the MOF synthesis or via post-synthetic modification (PSM).[9,10] An isoreticular MOF can sometimes be synthesised under the same reaction conditions using a functionalised linker,[11] but very often the conditions must be optimised again. An additional functional group in the linker can also lead to a different reaction product due to changes in the solubility and/or coordination properties. Nevertheless, the tedious optimisation is often worthwhile because a functionalised MOF facilitates PSM. Especially amino-functionalised MOFs and their usage for PSM have resulted in many modified framework compounds.[9,12,13] Besides acetylation with anhydrides,[13,14] cyclic anhydrides[15] and carboxylic acid chlorides,[16] there are also known modification reactions with isocyanates,[17] aldehydes,[18] alkylbromides[19] and peptide coupling reagent.[20] The large pool of potential PSM reactions for amino-functionalised MOFs allows many possibilities to generate new, functionalised frameworks.

In this work, we present the results of the systematic investigation of the system $Bi^{3+}/TATB^{3-}/H_2O/DMF/CH_3OH$, which led to two different Bi-MOFs of the composition $[Bi_2(O)(OH)(TATB)]$ (CAU-35, $TATB^{3-}$ = 1,3,5-triazine-2,4,6-trisbenzoate, Scheme 1) and [Bi(TATB)] (CAU-7-TATB). The latter was also obtained using a functionalised linker with one amino group per linker molecule (CAU-7-TATB-NH_2), and this Bi-MOF was investigated in several PSM reactions.

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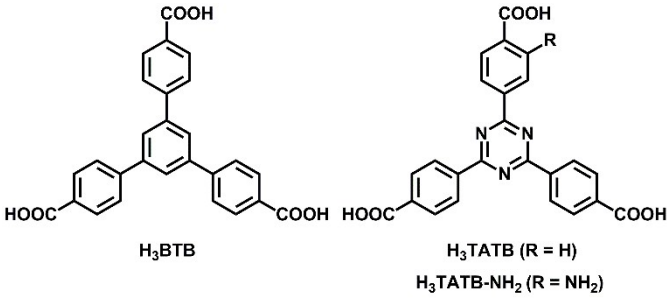

Scheme 1 Molecular structure of the organic linkers H_3BTB, H_3TATB and $H_3TATB\text{-}NH_2$.

Results and discussion

The systematic investigation of the system $Bi^{3+}/TATB^{3-}/H_2O/DMF/CH_3OH$ was carried out using our high-throughput set-up.[21] To study the influence of different reaction parameters on the product formation the molar ratio and concentration of starting materials, the solvent (-mixtures) and reaction temperatures/times were varied.

Depending on the reaction conditions, two different products were obtained using $Bi(NO_3)_3{\cdot}5H_2O$ and H_3TATB. CAU-35 is formed when water/DMF-mixtures and long reaction times are used in a conventional solvothermal synthesis. On the other hand, short reaction times and methanol/DMF-mixtures in a microwave-assisted synthesis led to CAU-7-TATB. The conditions for the synthesis of CAU-7-TATB-NH_2 are very similar.

CAU-35

During the high-throughput experiments with H_3TATB and bismuth(III) nitrate pentahydrate, a product with the composition $[Bi_2(O)(OH)(TATB)]$, denoted as CAU-35, was discovered. The crystal structure of this compound was successfully solved and refined from PXRD data. Details about the solution and refinement are given in the Supporting Information (page S20), the Rietveld plot is shown in Fig. 1.

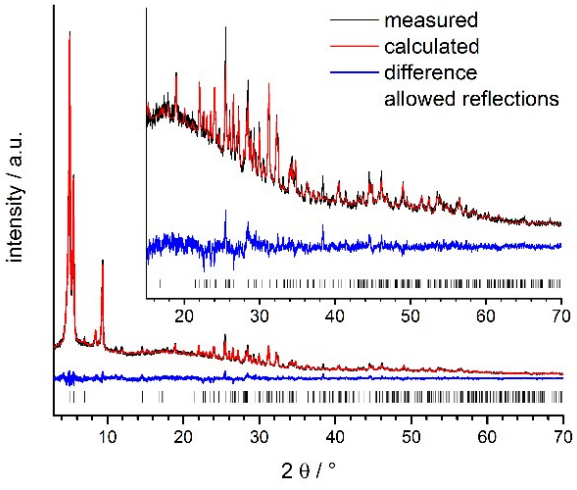

Fig. 1 Rietveld plot of the refinement of CAU-35. Measured and calculated PXRD data, the difference of both and the allowed reflections are shown in black, red, blue and as black bars, respectively.

In CAU-35, the structure is build up by a linear inorganic building unit (IBU) with BiO_7-polyhedra, which are connected to a chain of composition $\{Bi_2O_{6.5}\}$ (Fig. S22). The connection of these IBUs to a network is reminiscent to a distorted honeycomb net with one additional linker inside the distorted hexagonal pore (Fig. 2 and 3). According to the Rietveld analysis, two oxygen atoms are observed in the IBU of CAU-35 that are not part of a linker molecule. One is coordinating to four Bi^{3+} ions (μ_4-O^{2-} ion) and the other oxygen atom is bridging three Bi^{3+} ions (μ_3-OH^- ion). Since the structure is solved and refined from PXRD data, we were not able to unequivocally locate the position of the proton. Charge balance by dimethylammonium ions in the pores, which can be formed by hydrolysis of DMF during the synthesis, can be excluded based on the characterisation data (IR spectroscopy as well as TG and elemental analysis). The irregular, distorted shape of the BiO_7-polyhedra is caused by the lone electron pair of the Bi^{3+} ions.[22]

CAU-35 exhibits moderate sorption properties, with a specific BET surface area of 77 m^2/g and a micropore volume of 0.06 cm^3/g (Fig. S23). A detailed characterisation of this compound, including N_2 sorption, IR, TG and elemental analysis data, is given in the Supporting Information (page S26-S28).

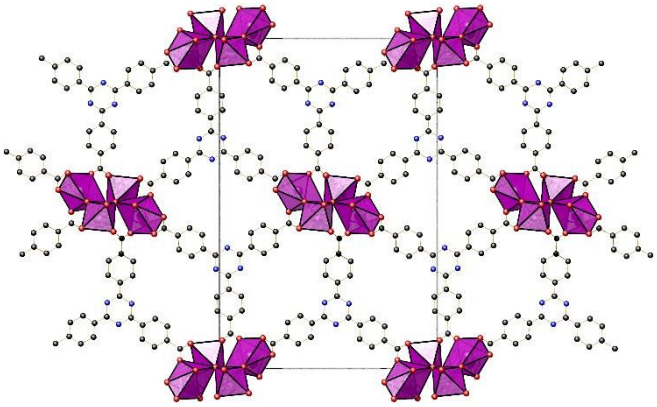

Fig. 2 Crystal structure of CAU-35 (view along [001]). The unit cell dimension is represented by the box.

CAU-7-TATB

$[Bi(TATB)]{\cdot}DMF{\cdot}6H_2O$ (CAU-7-TATB (*as*), *as* = as synthesised) was obtained employing H_3TATB and bismuth(III) nitrate pentahydrate using short reaction times (20 min) and a mixture of methanol and DMF as the solvent. In contrast to CAU-7-BTB, which was first obtained using H_3BTB as the linker (Scheme 1),[4] structural transformation upon activation of CAU-7-TATB (*as*) is observed. The PXRD pattern of CAU-7-TATB (*as*) is very similar to the one of CAU-7-BTB. Indexing of the PXRD pattern led to a monoclinic unit cell, which was confirmed by a LeBail fit (Table S1, Fig. S1). When the as synthesised sample is treated at 120 °C for 1 d, the crystal structure changes to the orthorhombic high temperature (*ht*) phase of CAU-7-TATB. High resolution PXRD data of CAU-7-

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TATB (*ht*) allowed a Rietveld refinement of the structure (Tab. S1, Fig. S3). To obtain a guest free sample of CAU-7-TATB (*ht*) activation was carried out in a glass capillary, which was heated at 120 °C under reduced pressure for 1 h. In comparison to the structure of CAU-7-BTB, in CAU-7-TATB (*ht*) (Fig. 3) less rotation of the benzoate groups is observed with respect to the central aromatic ring, and thus the rings are more co-planar. This observation is typical for triazine based linkers, due to the missing steric hindrance of the hydrogen atoms.[23] The analysis of the nitrogen sorption isotherm of CAU-7-TATB led to a specific BET surface area of 813 m^2/g and a micropore volume of 0.31 cm^3/g (Fig. S7). These are lower than the published values for CAU-7-BTB (A_{BET} = 1150 m^2/g, V_{mic} = 0.43 cm^3/g),[4] but correlate well with the theoretical values (A_{BET} = 867 m^2/g, V_{mic} = 0.32 cm^3/g), which are calculated using the program Materials Studio.[24]

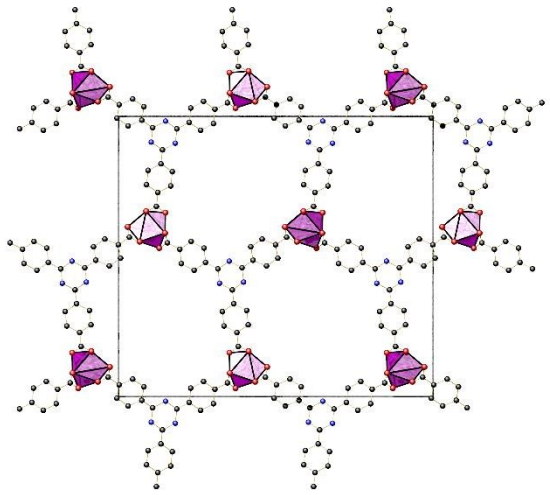

Fig. 3 Crystal structure of CAU-7-TATB (view along [001]). The unit cell dimension is represented by the box.

CAU-7-TATB-NH_2

Reactions carried out under very similar synthesis conditions to those of CAU-7-TATB with H_3TATB-NH_2 as the linker resulted in successful formation of the CAU-7 analogue [Bi(TATB-NH_2)] ·5H_2O·0.5DMF (CAU-7-TATB-NH_2), which is, to the best of our knowledge, the first example of a functionalised Bi-MOF. Whereas for CAU-7-TATB two different phases (*as* and *ht*) were discovered, for CAU-7-TATB-NH_2 only one phase with an orthorhombic crystal structure was observed (Table S4, Fig. S10). Since synthesis scale-up could not be carried out, several batches of CAU-7-TATB-NH_2 were synthesised under identical reaction conditions. In order to get sufficiently large amounts of the compound for a systematic PSM study, the exact same starting materials were used in every synthesis.

Although the characterisation of the different batches by PXRD, elemental- and thermogravimetric analysis, as well as the infrared spectroscopy did not indicate any impurity (Supporting Information, page S16-S17 and page S36-S38) large variation in the nitrogen adsorption properties (A_{BET} in a range of 104-627 m^2/g) were observed. To get insight into this effect, high resolution scanning electron microscope (SEM) micrographs were taken of two samples with significantly different BET surface areas. Surprisingly, no differences could be detected (Fig. S13-S16).

Post-synthetic modification of CAU-7-TATB-NH_2

The possibility of PSM reactions using CAU-7-TATB-NH_2 was explored using some typical literature procedures.[9] For this purpose eight synthesis batches of CAU-7-TATB-NH_2 were combined to ensure data consistency and all PSM reactions were performed using this mixture. CAU-7-TATB-NH_2 was treated with methanesulfonyl chloride, acetyl chloride, ethyl isocyanate, several anhydrides and two different sultones. After treatment with methanesulfonyl chloride and acetyl chloride, a clear solution was obtained. Since CAU-7-TATB-NH_2 is not stable against HCl, the reaction was performed in the presence of pyridine or triethyl amine to capture the HCl which is formed during the acetylation of the amino group. Nevertheless, dissolution of the material was observed. Different observations were made for the treatment of CAU-7-TATB-NH_2 with ethyl isocyanate. In this case, a degradation of the structure was observed (Fig. S33). In all three cases, it remains unclear why the degradation takes place.

In contrast, the treatment with anhydrides like acetic anhydride and valeric anhydride was successful and resulted in the formation of CAU-7-TATB-NH_2-AA and CAU-7-TATB-NH_2-VA, respectively (Scheme 2). Both MOFs maintain their structure according to PXRD data (Fig. S32). The degree of conversion was determined by comparing the relative integrals in the ^{1}H-NMR-spectra after digestion of the MOF (Fig. S26 and S27). The degree of conversion drops from 79 % for CAU-7-TATB-NH_2-AA to 47 % for CAU-7-TATB-NH_2-VA, which may be attributed to the longer alkyl chain of valeric anhydride.

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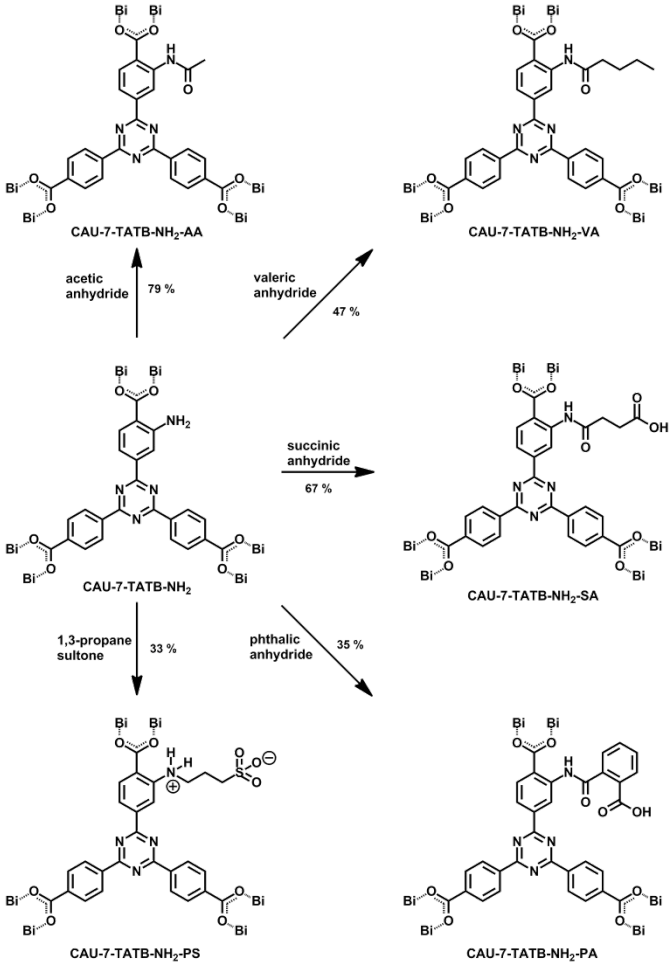

Scheme 2 Post-synthetic modification of CAU-7-TATB-NH_2 with the respective anhydrides and 1,3-propane sultone. Degree of conversion in %.

Despite the limited stability of CAU-7-TATB-NH_2 towards acids, four reactions were carried out to introduce pendant carboxylic and sulfonic acid groups into the framework. By treating CAU-7-TATB-NH_2 with cyclic anhydrides such as succinic and phthalic anhydride, two functionalised MOFs with free carboxylic acid groups were obtained (Scheme 2). Succinic anhydride resulted in the formation of CAU-7-TATB-NH_2-SA with 67 % conversion and phthalic anhydride gave CAU-7-TATB-NH_2-PA with 35 % conversion (Fig. S28 and S29). To introduce pendant sulfonic acid groups into the framework, ring-opening reactions using 1,3-propane sultone or 1,4-butane sultone were performed. In both cases, the MOF maintained its structure after the reaction but only the treatment with 1,3-propane sultone led to a conversion of the amino groups. The respective CAU-7-TATB-NH_2-PS was obtained with a conversion of 33 % (Fig. S30). It should be mentioned that the sulfonic acid group within the framework most likely might be deprotonated due to internal neutralisation. The investigation of the same PSM reaction on a different MOF proved that a zwitterionic form is preferred and the acidity is attributed to the ammonium group.[25] Nevertheless, these results show that CAU-7-TATB-NH_2 is capable of bearing acidic groups within the pores. Analytical data (^{1}H-NMR, PXRD, TGA, elemental analysis, IR) for all modified MOFs are available in the Supporting Information (page S29-S38).

Experimental

Chemicals and experimental details

The chemicals were purchased from Aldrich, Alfa Aesar or Walter CMP and used without further purification. Syntheses were carried out under solvothermal conditions in a Biotage Initiator microwave oven or in self-made high-throughput autoclaves with in PTFE inserts of 2 mL volume.[21]

Powder X-ray diffraction (PXRD) was performed on a STOE Stadi P Combi (λ = 1.5406 Å) equipped with a MYTHEN detector. FOX[26] was used for structure solution from PXRD data and TOPAS Academic 4.1[27] for LeBail fits and Rietveld refinement.

Sorption measurements were performed on a BELsorp max or BELsorp mini, infrared spectroscopy on a Bruker Alpha-P spectrometer and elemental analyses on a HEKAtech Euro Elemental Analyzer. The scanning electron microscopy (SEM) experimentswere performed on a *Jeol JSM-6500F* with EDX-Detector and *Inca*-software (*Oxford Instruments*).

NMR spectra were recorded on Bruker DRX 500 or AV 600 instruments and assignments were supported by COSY, HSQC and HMBC. Even when spectra were obtained as broad-band decoupled ^{13}C-NMR, the type of ^{13}C signal is always listed as singlet, doublet, etc. Degree of conversion by post-synthetic modification reaction was determined by comparing the relative integrals in ^{1}H-NMR-spectra of digested material. Digestion was achieved by adding a mixture of DMSO-d_6 and DCl (37 %) to the MOF.

Crystallographic information files

The crystallographic information is available in the Cambridge Structural Database (CSD) as CCDC 1549690 (CAU-7-TATB (*ht*)) and CCDC 1549691 (CAU-35).

Syntheses of the organic linkers

The synthesis of H_3TATB[28] and functionalised H_3TATB-NO_2[29] were performed according to literature procedures. The nitro-group of H_3TATB-NO_2 was reduced by sodium dithionite to obtain H_3TATB-NH_2. For synthetic details and characterisation see Supporting Information.

Syntheses of the metal-organic frameworks

Synthesis of [Bi(TATB)] (CAU-7-TATB): H_3TATB (30.0 mg, 68.0 µmol) and ground $Bi(NO_3)_3 \cdot 5\ H_2O$ (28.7 mg, 59.2 µmol) were mixed in a 30 mL glass vial and MeOH (6 mL) and DMF (6 mL) were added. The sealed vial was shaken and heated in a microwave-assisted synthesis at 120 °C for 20 min while stirring with 600 rpm. The solid product was filtered off and washed with DMF (5 mL) and MeOH (5 mL). A white powder was obtained in a yield of 30.8 mg (55% based on H_3TATB). Phase purity was confirmed by PXRD (Fig. S1) and elemental

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analysis (calc. (%) for $BiC_{24}H_{12}N_3O_6 \cdot C_3H_7NO \cdot 6H_2O$: C 39.14, H 3.77, N 6.76; meas. (%): C 37.29, H 2.93, N 7.84).

Synthesis of [Bi(TATB-NH_2)] (CAU-7-TATB-NH_2): H_3TATB-NH_2 (100 mg, 219 µmol) and ground $Bi(NO_3)_3 \cdot 5\ H_2O$ (76.8 mg, 158 µmol) were mixed in a 30 mL glass vial and MeOH (10 mL) and DMF (10 mL) were added. The sealed vial was shaken and heated in a microwave-assisted synthesis at 120 °C for 20 min while stirring with 600 rpm. The solid product was filtered off and washed with DMF (5 mL) and MeOH (5 mL). A yellow powder was obtained in a yield of 118 mg (68% based on H_3TATB-NH_2). Phase purity was confirmed by PXRD (Fig. S10) and elemental analysis (calc. (%) for $BiC_{24}H_{13}N_4O_6 \cdot 0.5C_3H_7NO \cdot 5H_2O$: C 38.82, H 3.39, N 7.99; meas. (%): C 39.74, H 1.85, N 7.99).

Synthesis of [Bi_2(O)(OH)(TATB)] (CAU-35):
H_3TATB (5.0 mg, 11.3 µmol) and ground $Bi(NO_3)_3 \cdot 5\ H_2O$ (5.5 mg, 11.3 µmol) were mixed in a 2 mL PTFE inserts and H_2O (800 µL) and DMF (200 µL) were added. The autoclave was sealed and heated to 120 °C in 12 h. The temperature was kept for 36 h and subsequently the reactor was slowly cooled to room temperature in 60 h. The solid product was filtered off and washed with DMF (1 mL) and H_2O (1 mL). A white powder was obtained. Phase purity was confirmed by PXRD (Fig. S17) and elemental analysis (calc. (%) for $Bi_2C_{24}H_{13}N_3O_8 \cdot H_2O$: C 31.77, H 1.67, N 4.63; meas. (%): C 32.77, H 1.41, N 4.97).

Post-synthetic modification procedure

Prior to the modification reactions, CAU-7-TATB-NH_2 was dried for 12 h at 60 °C in a vacuum oven. 15 equivalents of the respective anhydride or sultone were added to a suspension of CAU-7-TATB-NH_2 (130 mg, 195 µmol) in dichloromethane (6 mL). The reaction mixture was stirred under reflux for 72 h. These conditions were chosen to ensure highest degree of conversion. The solid was separated by centrifugation and washed with dichloromethane (2 x 10 mL), ethanol (2 x 10 mL) and water (2 x 10 mL). After drying for 4 d at 60 °C in a vacuum oven, 10 mg of the solid was digested with a mixture of DMSO-d_6 (595 µL) and DCl (37 %, 5 µL). The conversion was determined by ^{1}H-NMR spectroscopy (see Supporting Information).

Conclusions

In summary, we used the triazine-based H_3TATB linker for the synthesis of two new Bi-MOFs. Depending on the solvent mixture and the reaction time, either a MOF with CAU-7 structure (CAU-7-TATB) or a new MOF (CAU-35) was obtained. The structure of CAU-35 was successfully solved and refined from PXRD data, the structure of CAU-7-TATB was confirmed by a Rietveld analysis of the PXRD data. Additionally, a new amino-substituted H_3TATB linker (H_3TATB-NH_2) was synthesised and used for the synthesis of the first functionalised Bi-MOF, denoted CAU-7-TATB-NH_2. This MOF was successfully treated with acetic anhydride, valeric anhydride, succinic anhydride, phthalic anhydride and 1,3-propane sultone to give the respective modified Bi-MOFs with degrees of conversion varying from 33 to 79 %.

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Notes and references

1 H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, *Science*, 2013, **341**, 1230444.
2 A. C. McKinlay, R. E. Morris, P. Horcajada, G. Férey, R. Gref, P. Couvreur and C. Serre, *Angew. Chem.*, 2010, **122**, 6400–6406, *Angew. Chem. Int. Ed.*, **49**, 6260–6266.
3 Y. Yang, R. Ouyang, L. Xu, N. Guo, W. Li, K. Feng, L. Ouyang, Z. Yang, S. Zhou and Y. Miao, *J. Coord. Chem.*, 2014, **68**, 379–397.
4 M. Feyand, E. Mugnaioli, F. Vermoortele, B. Bueken, J. M. Dieterich, T. Reimer, U. Kolb, D. de Vos and N. Stock, *Angew. Chem.*, 2012, **124**, 10519–10522, *Angew. Chem. Int. Ed.*, 2012, **51**, 10373–10376.
5 M. Savage, S. Yang, M. Suyetin, E. Bichoutskaia, W. Lewis, A. J. Blake, S. A. Barnett and M. Schröder, *Chem. - Eur. J.*, 2014, **20**, 8024–8029.
6 A. K. Inge, M. Köppen, J. Su, M. Feyand, H. Xu, X. Zou, M. O'Keeffe and N. Stock, *J. Am. Chem. Soc.*, 2016, **138**, 1970–1976.
7 a) G. Wang, Y. Liu, B. Huang, X. Qin, X. Zhang and Y. Dai, *Dalton Trans.*, 2015, **44**, 16238–16241; b) G. Wang, Q. Sun, Y. Liu, B. Huang, Y. Dai, X. Zhang and X. Qin, *Chem. - Eur. J.*, 2015, **21**, 2364–2367.
8 M. Feyand, M. Köppen, G. Friedrichs and N. Stock, *Chem. - Eur. J.*, 2013, **19**, 12537–12546.
9 S. M. Cohen, *Chem. Rev.*, 2012, **112**, 970–1000.
10 a) S. M. Cohen, *J. Am. Chem. Soc.*, 2017, **139**, 2855–2863; b) K. K. Tanabe and S. M. Cohen, *Chem. Soc. Rev.*, 2011, **40**, 498–519.
11 M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469–472.
12 A. Klinkebiel, N. Reimer, M. Lammert, N. Stock and U. Lüning, *Chem. Commun.*, 2014, **50**, 9306–9308.
13 H. Hintz and S. Wuttke, *Chem. Mater.*, 2014, **26**, 6722–6728.
14 a) S. J. Garibay and S. M. Cohen, *Chem. Commun.*, 2010, **46**, 7700–7702; b) K. K. Tanabe, Z. Wang and S. M. Cohen, *J. Am. Chem. Soc.*, 2008, **130**, 8508–8517; c) Z. Wang, K. K. Tanabe and S. M. Cohen, *Inorg. Chem.*, 2009, **48**, 296–306.
15 a) S. J. Garibay, Z. Wang and S. M. Cohen, *Inorg. Chem.*, 2010, **49**, 8086–8091; b) K. K. Tanabe and S. M. Cohen, *Angew. Chem.*, 2009, **121**, 7560–7563, *Angew. Chem. Int. Ed.*, **48**, 7424–7427.

View Article Online
DOI: 10.1039/C7DT01744H

16 a) A. Modrow, D. Zargarani, R. Herges and N. Stock, *Dalton Trans.*, 2012, **41**, 8690–8696; b) M. Savonnet, S. Aguado, U. Ravon, D. Bazer-Bachi, V. Lecocq, N. Bats, C. Pinel and D. Farrusseng, *Green Chem.*, 2009, **11**, 1729.
17 a) S. Bernt, V. Guillerm, C. Serre and N. Stock, *Chem. Commun.*, 2011, **47**, 2838–2840; b) E. Dugan, Z. Wang, M. Okamura, A. Medina and S. M. Cohen, *Chem. Commun.*, 2008, 3366–3368.
18 a) A. D. Burrows and L. L. Keenan, *CrystEngComm*, 2012, **14**, 4112; b) C. J. Doonan, W. Morris, H. Furukawa and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 9492–9493; c) M. J. Ingleson, J. P. Barrio, J.-B. Guilbaud, Y. Z. Khimyak and M. J. Rosseinsky, *Chem. Commun.*, 2008, 2680–2682.
19 K. M. L. Taylor-Pashow, J. Della Rocca, Z. Xie, S. Tran and W. Lin, *J. Am. Chem. Soc.*, 2009, **131**, 14261–14263.
20 H. Hintz and S. Wuttke, *Chem. Commun.*, 2014, **50**, 11472–11475.
21 N. Stock and S. Biswas, *Chem. Rev.*, 2012, **112**, 933–969.
22 A. C. Wibowo, M. D. Smith and H.-C. Zur Loye, *Chem. Commun.*, 2011, **47**, 7371–7373.
23 A. Klinkebiel, O. Beyer, B. Malawko and U. Lüning, *Beilstein J. Org. Chem.*, 2016, **12**, 2267–2273.
24 a) *Materials Studio 5.5.3*, Accelrys Software Inc., 2010; b) T. Düren, F. Millange, G. Férey, K. S. Walton and R. Q. Snurr, *J. Phys. Chem. C*, 2007, **111**, 15350–15356.
25 H. Liu, F.-G. Xi, W. Sun, N.-N. Yang and E.-Q. Gao, *Inorg. Chem.*, 2016, **55**, 5753–5755.
26 V. Favre-Nicolin and R. Černý, *J. Appl. Crystallogr.*, 2002, **35**, 734–743.
27 A. Coelho, *TOPAS Academic 4.1*, Coelho Software, 2007.
28 M. Krüger, H. Reinsch, A. K. Inge and N. Stock, *Microporous Mesoporous Mater.*, 2017, **249**, 128-136.
29 E. Mühlbauer, A. Klinkebiel, O. Beyer, F. Auras, S. Wuttke, U. Lüning and T. Bein, *Microporous Mesoporous Mater.*, 2015, **216**, 51–55.

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