Amino Substituted $Cu_3(btc)_2$: A New Metal-Organic Framework with a Versatile Functionality

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SUPPORTING INFORMATION

Overview

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Experimental Methods

General

Starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Alfa Aesar, Grüssing, Merck, Inc., and others).

NMR spectra were acquired using a Bruker AVANCE 400, a Bruker Fourier 300 or a Varian Gemini-200BB spectrometer.

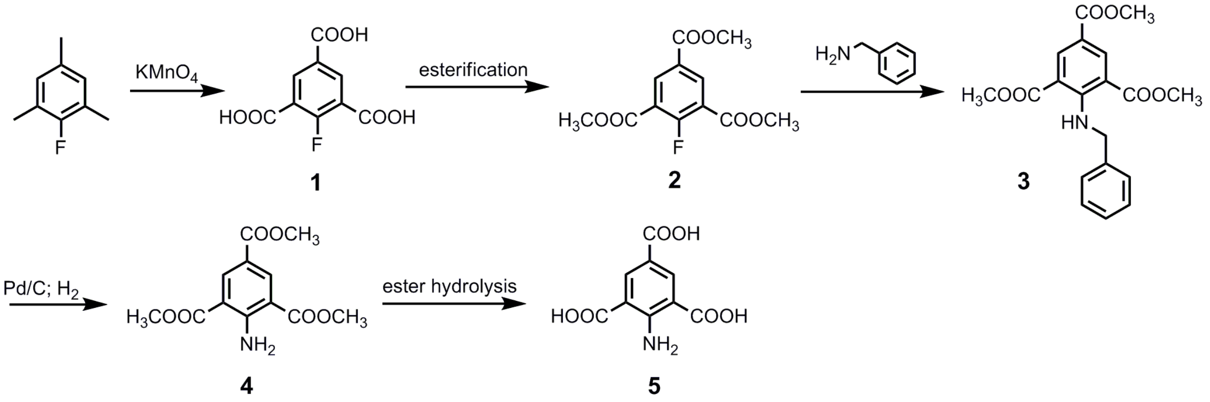
Infrared spectra were acquired using a Bruker Vertex ATR-IR and FT-IR spectrometer.

Powder X-ray diffraction patterns were recorded at room temperature with a PANalytical X'Pert Pro PW3040/60 reflexion-powder diffractometer using Cu Kα radiation (45 kV, 40 mA; counting time: 74 s; steps: 0.013° (2θ)).

Thermal analysis (thermogravimetry (TG)/mass spectrometry (MS)) was conducted under oxygen/argon (20/80) flow (20 mL min^{-1}) with a NETZSCH STA 449 F3 Jupiter thermobalance coupled by capillary with an Aëolos QMS 403 mass spectrometer. The heating rate was 5 K min^{-1} up to 800 °C.

Nitrogen physisorption data were recorded with a Quantachrome QUADRASORB-SI-MP at 77 K. The specific surface area was calculated from the adsorption branch in the relative pressure interval from 0.001 to 0.025 using the Brunauer-Emmett-Teller (BET) method. The micro pore volume was estimated from the quantity of gas adsorbed at a relative pressure of 0.18. Volumetric hydrogen physisorption data were recorded at 77 K on a Quantachrome Autosorb 1-MP (purity of helium and hydrogen: 99.999%). Carbon dioxide and methane physisorption data were recorded on a Quantachrome Autosorb iQ (purity of carbon dioxide: 99.5%, purity of methane: 99.9995%). High pressure methane and carbon dioxide physisorption data were recorded with BELSORP High Pressure Gas Adsorption at 298 K. High pressure hydrogen physisorption was measured with the same instrument at 77 K.

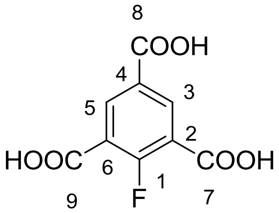
Synthesis of the Linker



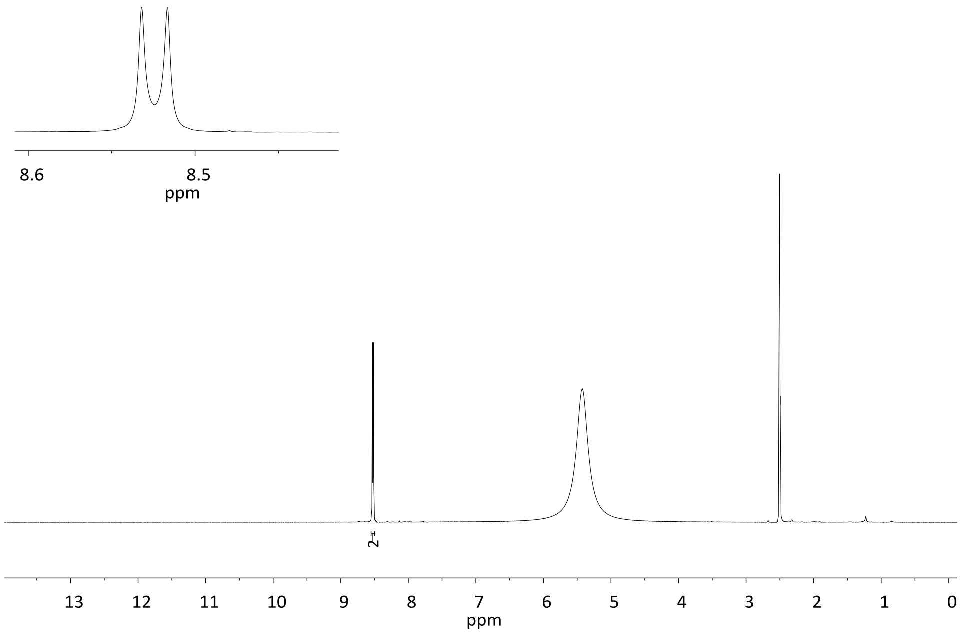
The synthesis of (**1**) to (**3**) was carried out according to a literature procedure.[1]

*2-Fluoro-1,3,5-benzenetricarboxylic acid (**1**).*

10.0 g (72.4 mmol) of 2-flouro-1,3,5-trimethylbenzene were emulsified in 530 mL boiling water. 53.2 g (337 mmol) of potassium permanganate were mixed with 42.6 g (173 mmol) of magnesium sulphate heptahydrate and added to the refluxing solution in five portions over a period of 72 h. The manganese(IV) oxide was removed by filtration and treated twice with 250 mL boiling water. The combined aqueous solutions were concentrated in vacuum to 300 mL and stored over night at 6 °C. The resulting inorganic precipitate was removed by filtration and the filtrate was concentrated in vacuum to 200 mL. The solution was then acidified with sulphuric acid (50%) up to pH=3.5 to give 6.82 g (29.9 mmol, yield: 41%) of a colourless powder.



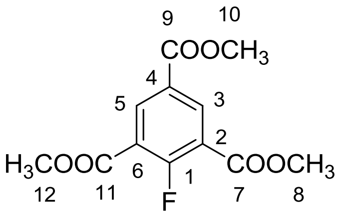
M = 228.13 g/mol



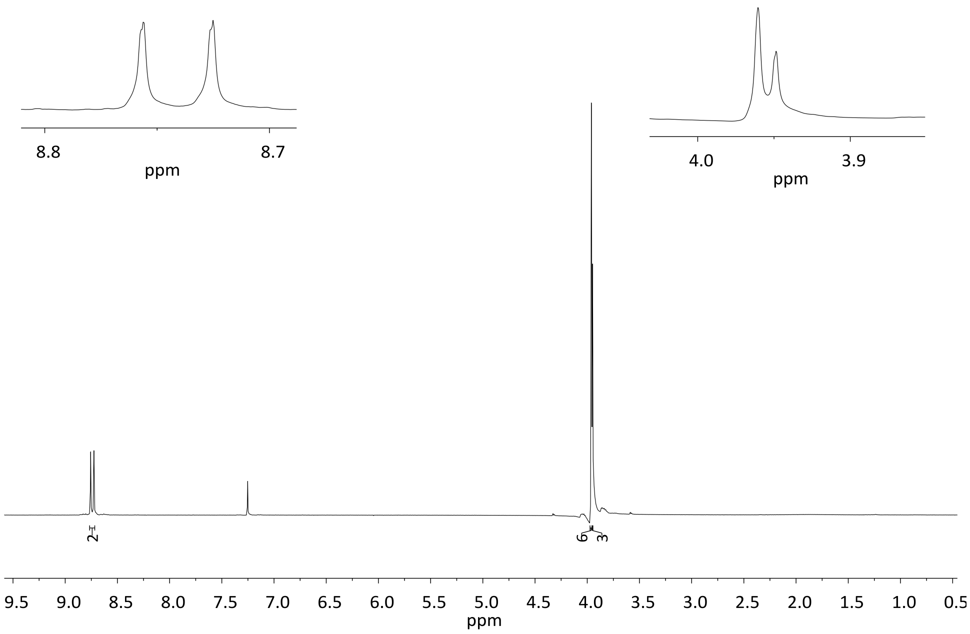
^{1}H-NMR (DMSO-*d6*, 400 MHz): δ (ppm) = 8.52 (*d*, $^4J_{H,F}$ = 6.1 Hz, 2H, H-3/H-5).
Further signals: δ (ppm) = 2.50 (*m*, DMSO); 5.42 (*s*, H_2O).
IR (FT-IR, KBr disk): ν (cm^{-1}) = 3421, 3096, 2361, 2342, 1701, 1607, 1559, 1471, 1431, 1398, 1272, 1233, 1214, 1181, 1112, 983, 939, 910, 812, 791, 768, 691, 664, 619.
[m/z]$^+$ = 228

As the solubility of (**1**) was very weak in all common solvents ^{13}C NMR studies could not be carried out.

*2-Fluoro-1,3,5-benzenetricarboxylic acid trimeythl ester (**2**).*
6.99 g (30.6 mmol) of (**1**) were refluxed in 80 mL methanol and 1.6 mL sulfuric acid (95%) for 6 h. The solution was concentrated in vacuum to 20 mL, poured in 400 mL water and neutralized with saturated sodium bicarbonate solution. The precipitated product was filtered to give 4.27 g (15.8 mmol, yield: 52%) of a colourless powder.

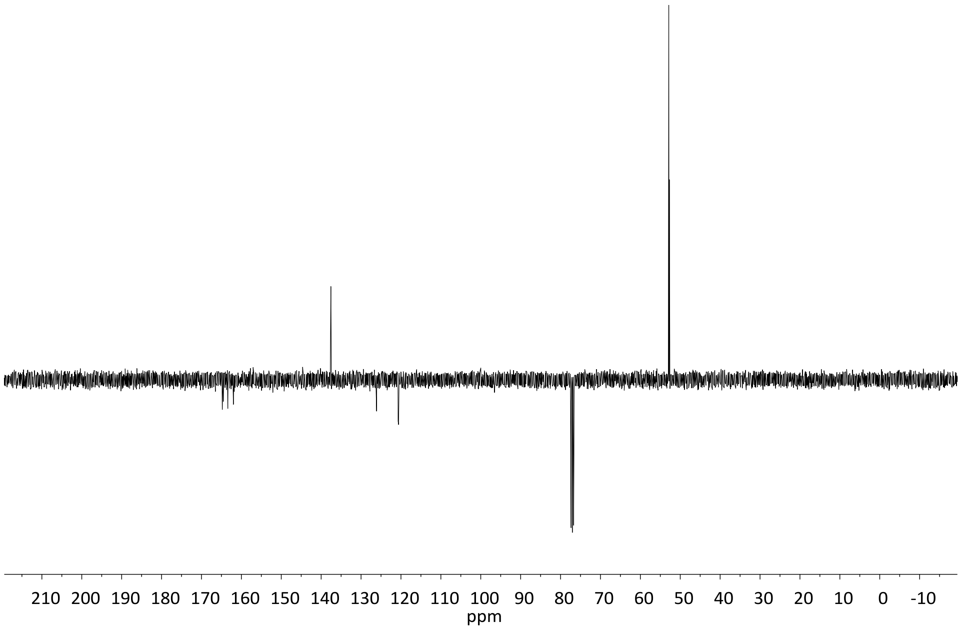


M = 270.21 g/mol



^{1}H-NMR (CDCl$_3$, 200 MHz): δ (ppm) = 8.74 (*d*, $^4J_{H,F}$ = 6.2 Hz, 2H, H-3/H-5); 3.96 (*s*, 6H, H-8/ H-12); 3.95 (*s*, 3H, H-10) .

Further signals: δ (ppm) = 7.26 (*s*, CHCl$_3$).



^{13}C {^{1}H}-NMR ($CDCl_3$, 100.6 MHz): δ (ppm) = 164.8 (C-9); 163.5 (*d*, $^3J_{C,F}$ = 3.8 Hz, C-7/C-11); 163.4 (164.6/162.1, *d*, $^1J_{C,F}$ = 255 Hz, C-1); 137.7 (*d*, ^3J = 2.9 Hz, C-3/C-5); 126.3 (*d*, $^4J_{C,F}$ = 4.6 Hz, C-4); 120.8 (*d*, $^2J_{C,F}$ = 11.9 Hz, C-2/C-6); 53.0 (C-8/C-12); 52.9 (C-10).

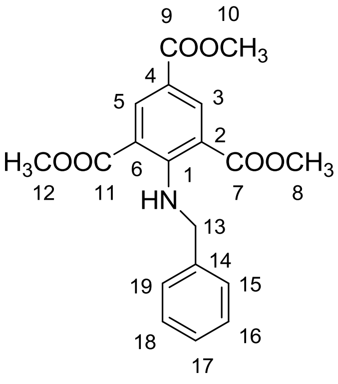
Further signals: δ (ppm) = 77.2 ($CHCl_3$).

IR (FT-IR, KBr disk): ν (cm^{-1}) = 3426, 3096, 3018, 2960, 2847, 1730, 1611, 1468, 1435, 1342, 1274, 1238, 1213, 1140, 1102, 1002, 894, 803, 764, 715, 675.

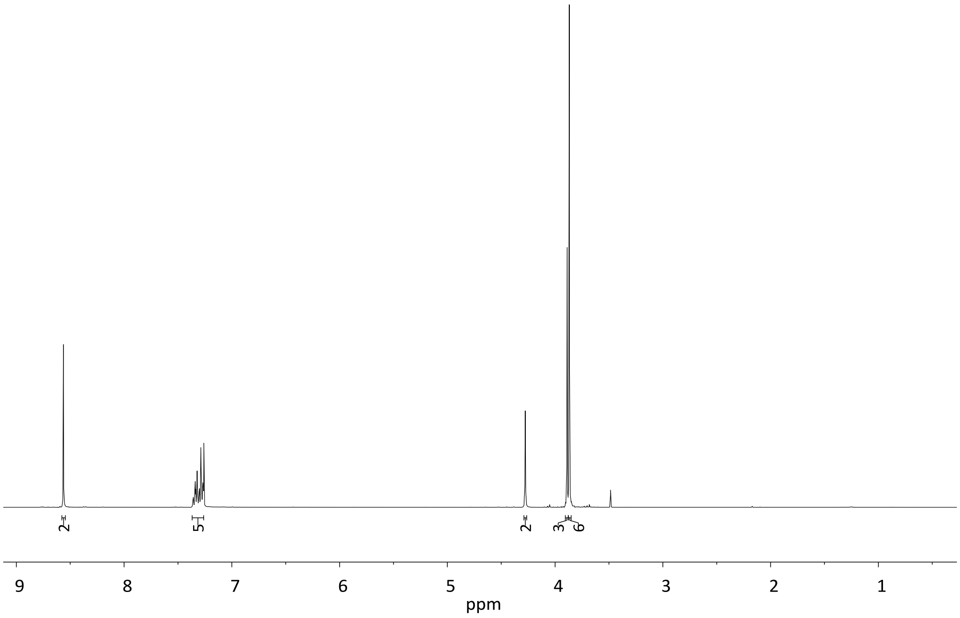
[m/z]$^+$ = 270

*2-[(Phenylmethyl)amino]-1,3,5-benzenetricarboxylic acid trimethyl ester (**3**).*

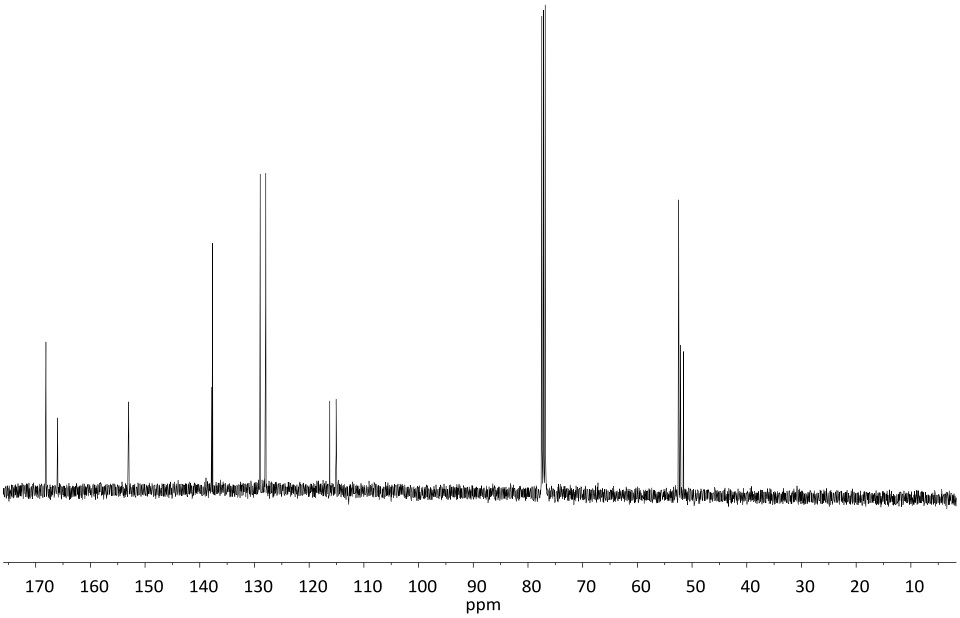
4.22 g (15.7 mmol) of (**2**) were dissolved in a solution of 60 mL methanol, 30 mL dioaxane and 9.27 mL benzylamine. After stirring for 10 min at room temperature the mixture was kept in an oven at 40 °C for 3 h. The solvents were removed under reduced pressure and the precipitate was treated with diluted hydrochloric acid (1 M). After drying in vacuum 5.37 g (15.0 mmol, yield: 96%) of a colourless crystalline powder were obtained.



M = 357.36 g/mol



^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) = 8.65 (*s*, 2H, H-3/H-5); 7.34-7.26 (*m*, 5H, H-15 bis H-19); 4.28 (s, 2H, H-13); 3.89 (s, 3 H, H-10); 3.87 (*s*, 6H, H-8/H-12).
Further signals: δ (ppm) = 7.26 (*s*, $CHCl_3$).

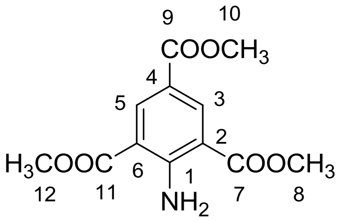


^{13}C {^{1}H}-NMR ($CDCl_3$, 100.6 MHz): δ (ppm) = 168.1 (C-7/C-11); 166.0 (C-9); 152.2 (C-1); 137.8 (C-14); 137.7 (C-3/C-5); 128.9, 128.0, 127.9 (C-15 to C-19); 116.2 (C-4); 115.0 (C-2/C-6); 52.4 (C-8/C-12); 52.1 (C-10); 51.5 (C-13).
Further signals: δ (ppm) = 77.2 ($CHCl_3$).

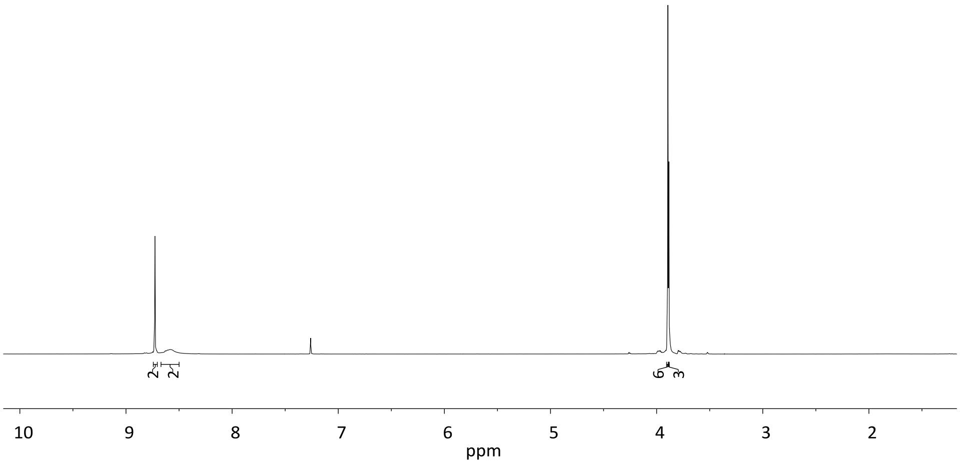
IR (FT-IR, KBr disk): *ν* (cm^{-1}) = 3251, 3091, 2948, 2868, 1708, 1684, 1603, 1582, 1522, 1496, 1455, 1430, 1409, 1326, 1238, 1194, 1175, 1134, 1079, 1009, 937, 799, 765, 717, 681, 665.
[m/z]$^+$ = 357

*2-Amino-1,3,5-benzenetricarboxylic acid trimethyl ester (**4**).*

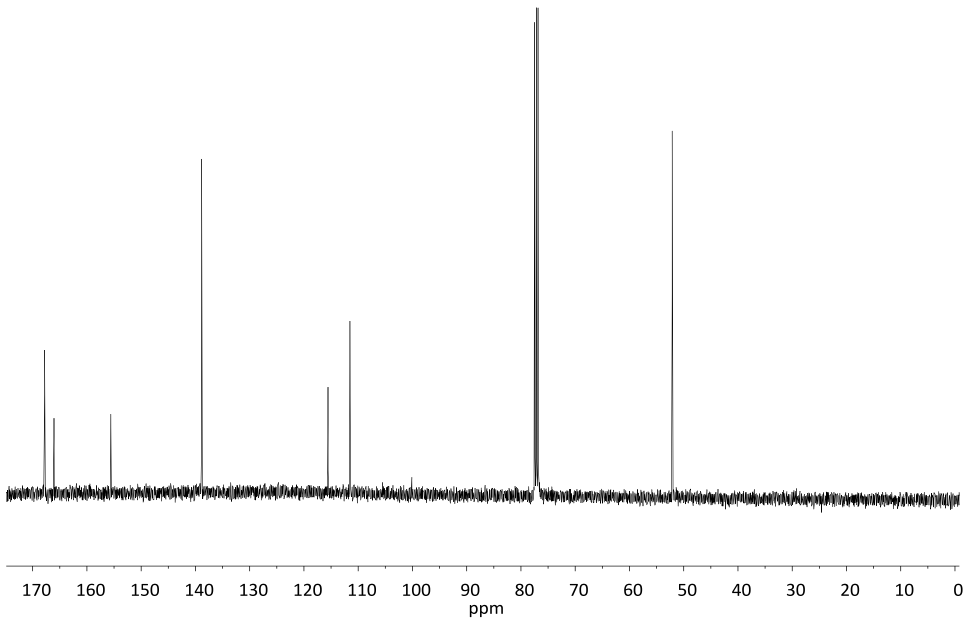
The synthesis of (**4**) was carried out in analogy of a literature procedure.[2] 5.30 g (14.8 mmol) of (**3**) in a solution of 180 mL tetrahydrofuran and 60 mL 2-propanol, containing 1.48 g palladium on activated charcoal (10%), were hydrogenated using a hydrogen balloon (~2 kg of pressure). After 48 h the mixture was filtered over a celite, washed with dichloromethane and the solvent was evaporated in vacuum to give 3.21 g (12.0 mmol, yield: 71%) of a colourless powder.



M =267.23 g/mol



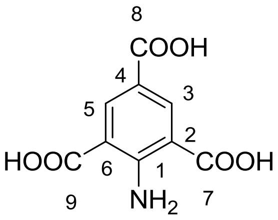
^{1}H-NMR (CDCl$_3$, 200 MHz): *δ* (ppm) = 8.73 (*s*, 2H, H-3/H-5); 8.58 (*s*, 2H, NH$_2$); 3.89 (*s*, 6H, H-8, H-12); 3.89 (*s*, 3H, H-10) .
Further signals: *δ* (ppm) = 7.26 (*s*, CHCl$_3$).



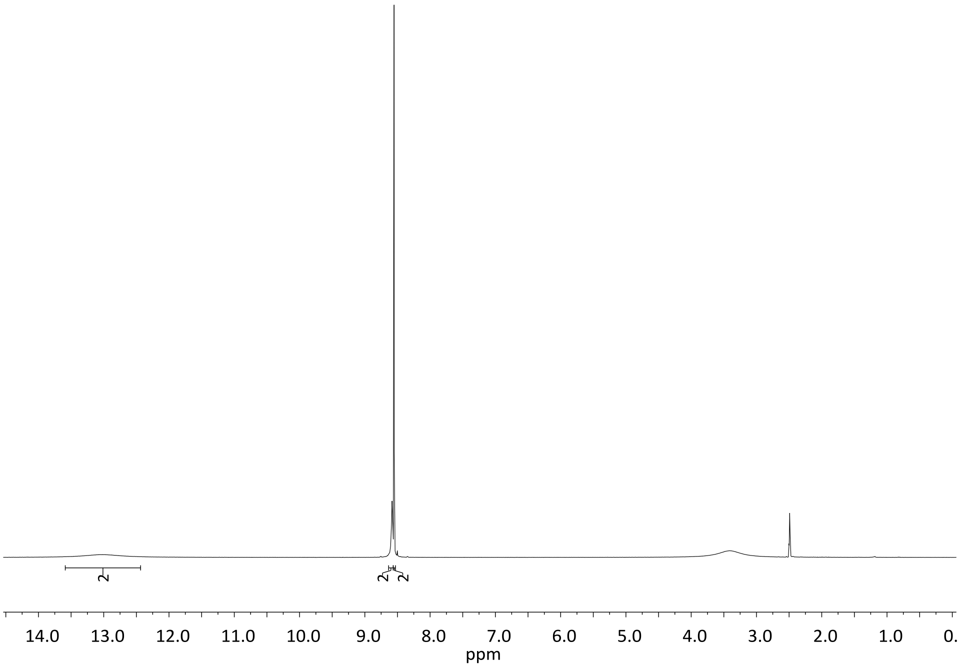
^{13}C {^{1}H}-NMR ($CDCl_3$, 100.6 MHz): δ (ppm) = 167.7 (C-7/C-11); 166.0 (C-9); 155.5 (C-1); 138.8 (C-3/C-5); 115.5 (C-4); 111.4 (C-3/C-5); 52.1 (C-8/C-12); 52.1 (C-10).
Further signals:δ (ppm) = 77.2 ($CHCl_3$).
IR (FT-IR, KBr disk): ν (cm^{-1}) = 3442, 3335, 2997, 2953, 2848, 1714, 1682, 1621, 1568, 1336, 1282, 1233, 1145, 1069, 1004, 937, 810, 763, 721, 708, 694, 69.
$[m/z]^+$ = 267

*2-Amino-1,3,5-benzenetricarboxylic acid (NH_2btc) (**5**).*

2.95 g (11.0 mmol) of (**4**) were dissolved in 50 mL tetrahydrofuran, mixed with 200 mL water and 30 mL potassium hydroxide solution (2M). The mixture was treated with microwave irradiation at 120 °C for 45 min. The mixture was concentrated in vacuum to remove the organic phase and the aqueous phase was acidified with hydrochloric acid (32%) to give 2.43 g (10.8 mmol, yield: 98%) of a colourless powder.

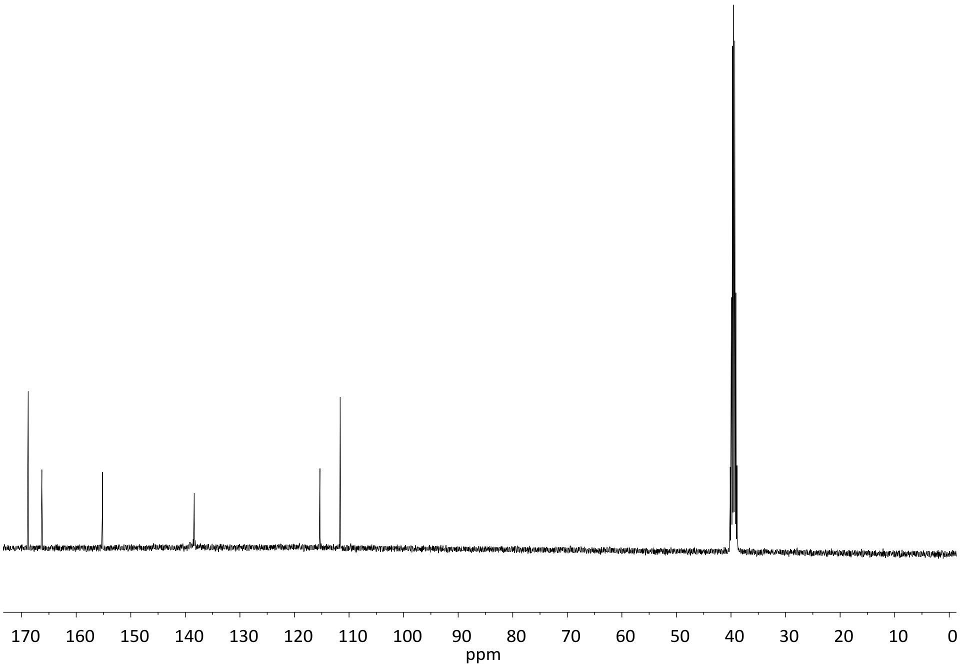


M = 225.16 g/mol



^{1}H-NMR (DMSO-*d*6, 400 MHz): *δ* (ppm) = 13.02 (*s*, 3H, H-7/H-8/H-9); 8.58 (*s*, 2H, NH_2); 8.55 (*s*, 2H, H-3/H-5).

Further signals: *δ* (ppm) = 2.50 (*m*, DMSO); 3.50 (s, H_2O).



^{13}C {^{1}H}-NMR (DMSO-*d*6, 100.6 MHz): *δ* (ppm) = 168.8 (C-7/C-9); 166.3 (C-8); 155.1 (C-1); 138.4 (C-3/C-5); 115.3 (C-4); 111.6 (C-3/C-5).

Further signals: *δ* (ppm) = 39.5 (DMSO).

IR (FT-IR, KBr disk): *ν* (cm^{-1}) = 3538, 3427, 3315, 3114, 1704, 1660, 1620, 1567, 1471, 1449, 1427, 1233, 1180, 1112, 1077, 939, 879, 812, 768, 746.

$[m/z]^+$ = 225

Synthesis of $Cu_3(NH_2btc)_2$ (UHM-30)

In a typical synthesis 510 mg (2.65 mmol) of 2-Amino-1,3,5- benzenetricarboxylic acid (**5**). and 1.03 g of $Cu(NO_3)_2 \cdot 3H_2O$ (4.26 mmol) were dissolved in 40 mL of DMA and 5 mL of H_2O in a 100 mL flask and heated to 85 °C for 42 h. The resulting green crystalline powder was collected by filtration, washed with DMA and dried in air to yield 950 mg of UHM-30. For activation the *as synthesized* form of the MOF was treated by soxhletextraction with ethanol for 20 h. After the solvent exchange the MOF was thermally activated in vacuum for 20 h at 120 °C.

Post Synthetic Modifications

In a typical synthesis 77.3 mg solvent exchanged $Cu_3(NH_2btc)_2$ (0.2 mmol $–NH_2$) were suspended in 2 mL $CHCl_3$ and treated with 1 to 20 equivalents of acetic anhydride at 55 °C for 24 h. After filtration the modified MOF was extensively washed with methanol and dried on air. For ^1H NMR studies 12 mg of the modified MOF were digested with DCl in DMSO-d_6. Generally, we needed two to three drops of DCl. That leads to slightly different pH-values of the sample solutions. Because the shift of the water protons signal in the NMR spectrum is dependent on the pH-value this results in different shifts for the water protons signal between 6 and 7 ppm. Similarly, 1 mg MOF was digested with HCl in methanol for ESI-MS.

Single-crystal X-ray crystallographic studies

X-ray single crystal diffraction data for $Cu_3(NH_2btc)_2$ (UHM-30) was collected on an Oxford Diffraction (Agilent Technologies) SuperNova diffractometer at 100(2) K with Cu Kα radiation (λ = 1.54184 Å) by ω scanning mode. The program CrysAlisPro[3] was used for integration of the diffraction profiles and absorption corrections. The structure was solved by direct methods using the SHELXS program of the SHELXTL package[4] and refined by full-matrix least-squares methods with SHELXL by successive difference Fourier syntheses against $|F|^2$. All non-hydrogen atoms – except the nitrogen atom of the amino group – were refined with anisotropic displacement parameters. The location of hydrogen atoms of the coordinated water molecules at the copper atoms of the paddle-wheel motif was not able to be assigned. The hydrogen atoms of the amino group could be located in the E map but the amino group has to be idealized by applying restraints.

Free solvent molecules (DMF and H_2O) in $Cu_3(NH_2btc)_2$ were highly disordered, and attempts to locate and refine the solvent peaks were unsuccessful. The diffuse electron densities resulting from the these residual solvent molecules were removed from the data set by using the SQUEEZE routine of PLATON.[5] The SQUEEZE routine detected voids with a total volume of 10794 $Å^3$ and sum-up the respective electron density to 2805 electrons per unit cell, compatible with a sum formula of $Cu_3(NH_2btc)_2 \cdot 3$ DMF $\cdot$ 5 H_2O.

Crystal data for $Cu_3(NH_2btc)$ (**UHM-30**): $C_{18}H_8Cu_3N_2O_{15}$, M = 682.85, turquoise block, 0.05 × 0.05 × 0.05 mm^3, cubic, space group *Fm*-3*m* (No. 225), a = 26.3336(2), V = 18261.3(2) $Å^3$, Z = 16, Dc = 0.993 g/cm^3, F000 = 8764, collected, 742 unique reflections. Final GooF = 2.407, R1 = 0.0985 [based on 582 reflections with $I > 2\sigma(I)$], wR2 = 0.3104 (based on all 742 reflections), 39 parameters, 1 restraint.

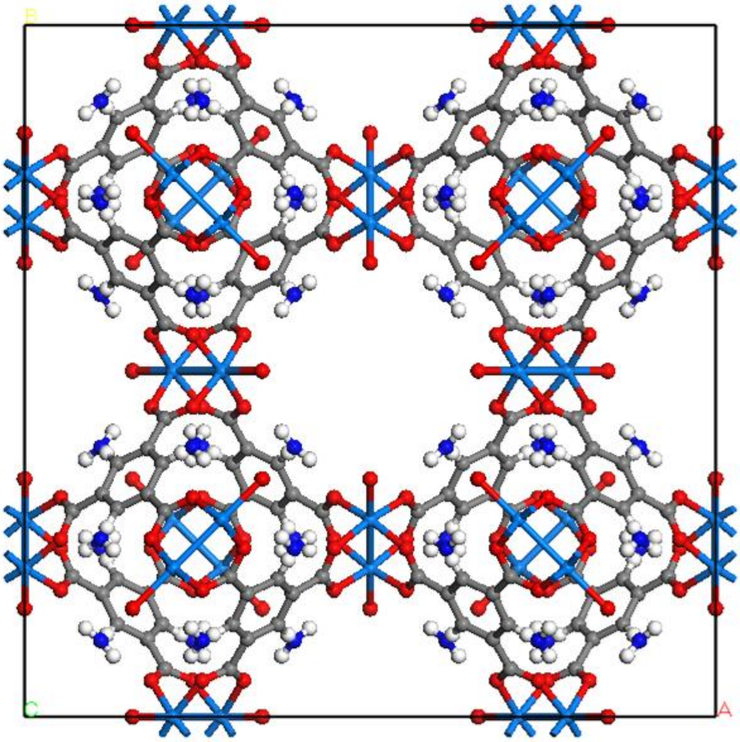


Figure S1: Unit cell of $Cu_3(NH_2btc)_2$ (UHM-30); gray: carbon, white: hydrogen, red: oxygen, light blue: copper, dark blue: nitrogen. The amino groups protrude into the cuboctahedral pores.

Characterisation of $Cu_3(NH_2btc)_2$ (UHM-30)

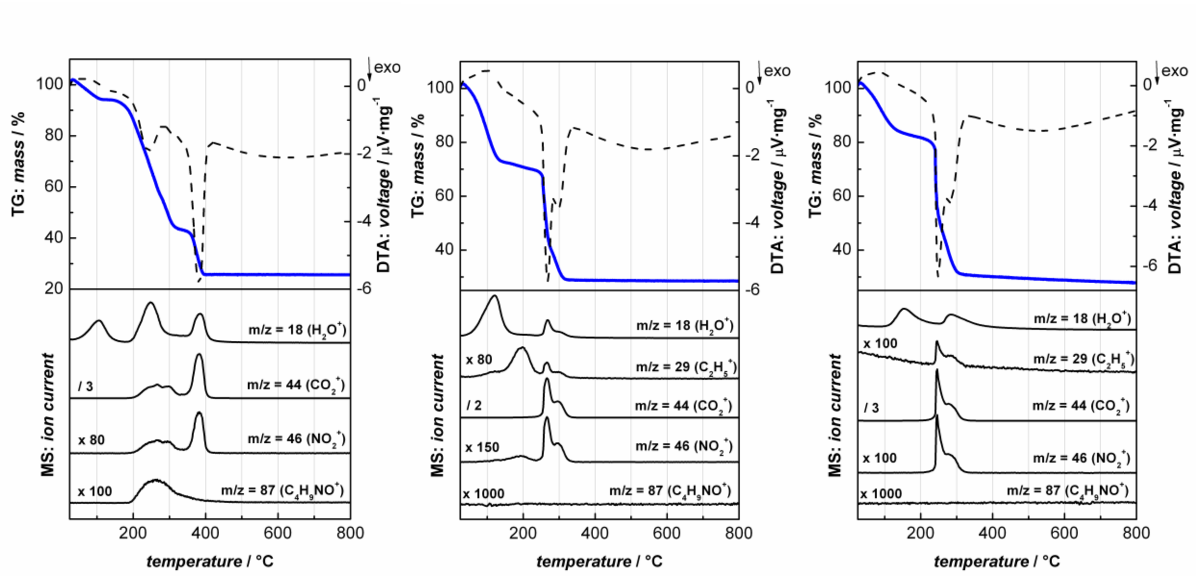


Figure S2: TG-DTA studies coupled with mass spectrometry. Left: $Cu_3(NH_2btc)_2$ as synthesized, middle: $Cu_3(NH_2btc)_2$ after solvent exchange, right: $Cu_3(NH_2btc)_2$ after thermal activation. The overall mass decrease of the as synthesized MOF can be roughly divided into three parts. Between 50 and 150 °C the dehydration of the material (m/z: 18) can be detected. The second step shows the detection of DMA (m/z: 87) in the as synthesized material between 200 and 350 °C. The third weight change occurs in the temperature interval of 320 to 400 °C and is accompanied by the detection of CO_2 (m/z: 44), water (m/z: 18) and NO_2 (m/z: 46), which are generated by the thermal decomposition of the network. The solvent exchanged material shows similar mass decrease steps. But one can tell that the DMA has successfully been exchanged by ethanol (C_2H_5: m/z: 29) which is detected between 150 and 250 °C. The mass decrease of the thermally activated MOF can be divided into two parts. During the first thermal interval (100 to 250 °C) the dehydration takes place, in the second interval the decomposition of the MOF is detected. This proves a successful thermal activation.

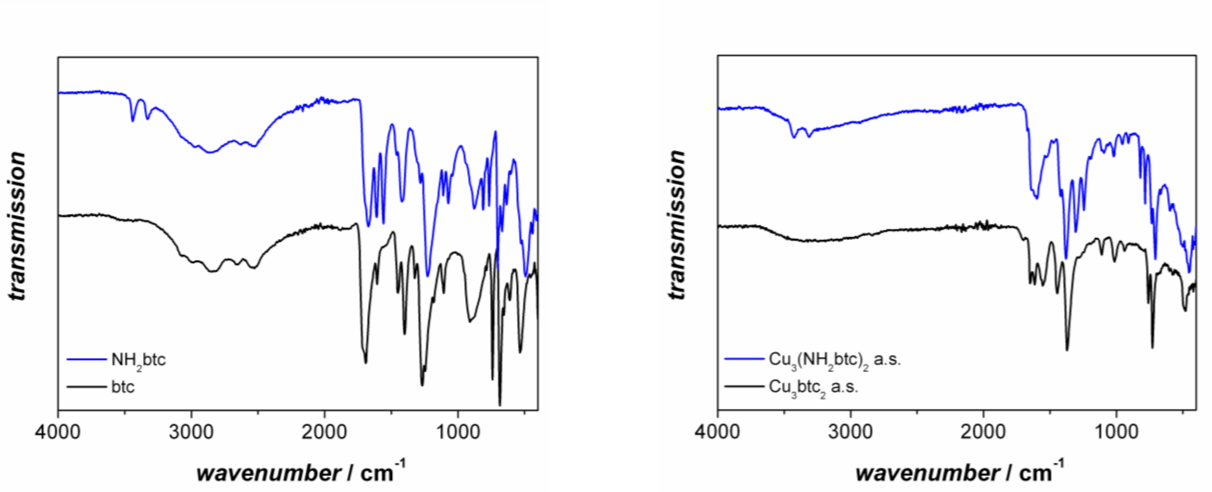


Figure S3: The IR spectra of NH_2btc (left) and $Cu_3(NH_2btc)_2$ (right) compared to btc and $Cu_3(btc)_2$ respectively confirm the presence of a primary amino group.

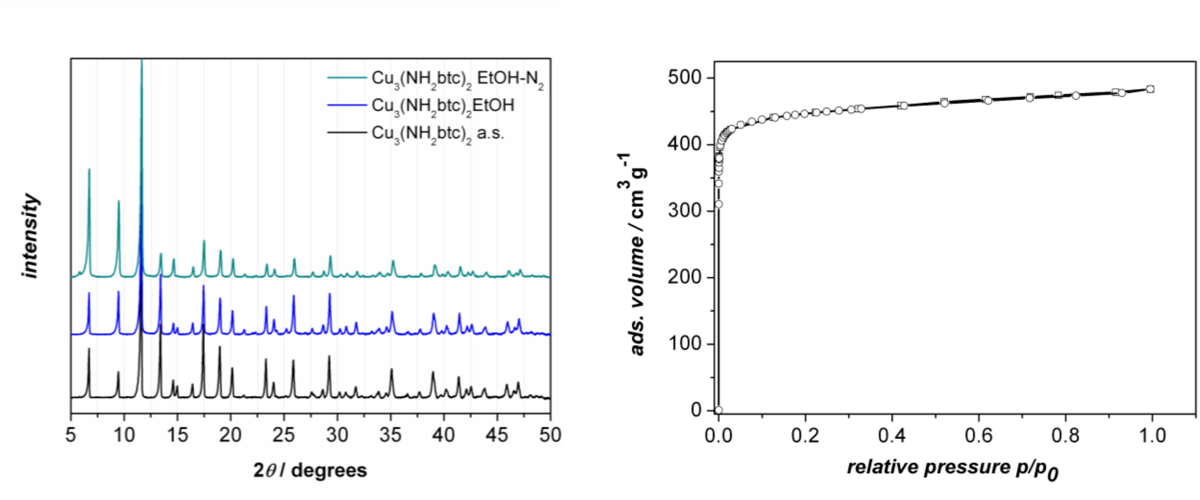


Figure S4: The powder diffraction pattern of $Cu_3(NH_2btc)_2$ (left) shows the remaining crytallinity of the MOF after solvent exchange (blue) and thermal activation (turquoise). The N_2 physisorption measurement (right) shows a type-I isotherm with a closed adsorption and desorption branch

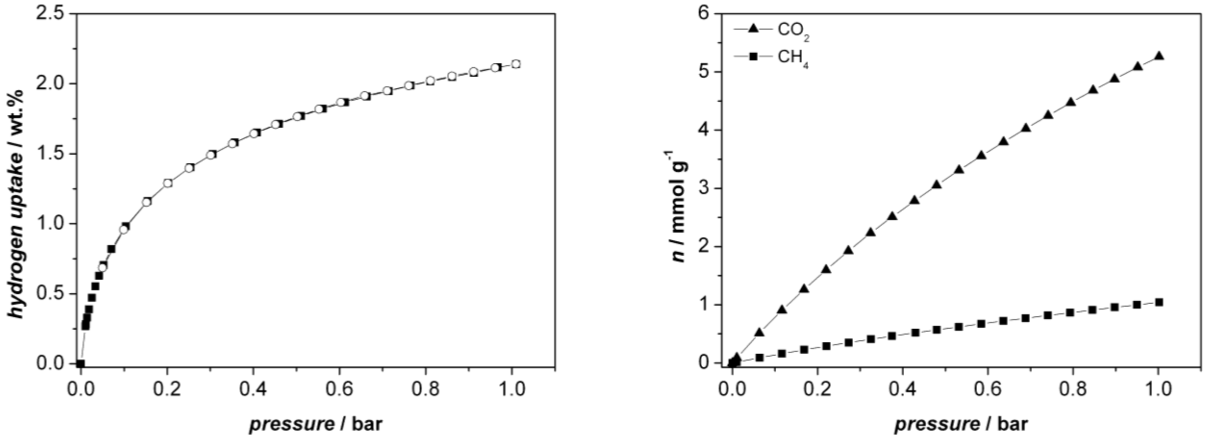


Figure S5: 1 bar H_2 sorption measurement at 77 K (left) and CO_2 and CH_4 adsorption measurements of $Cu_3(NH_2btc)_2$ at 298 K (right).

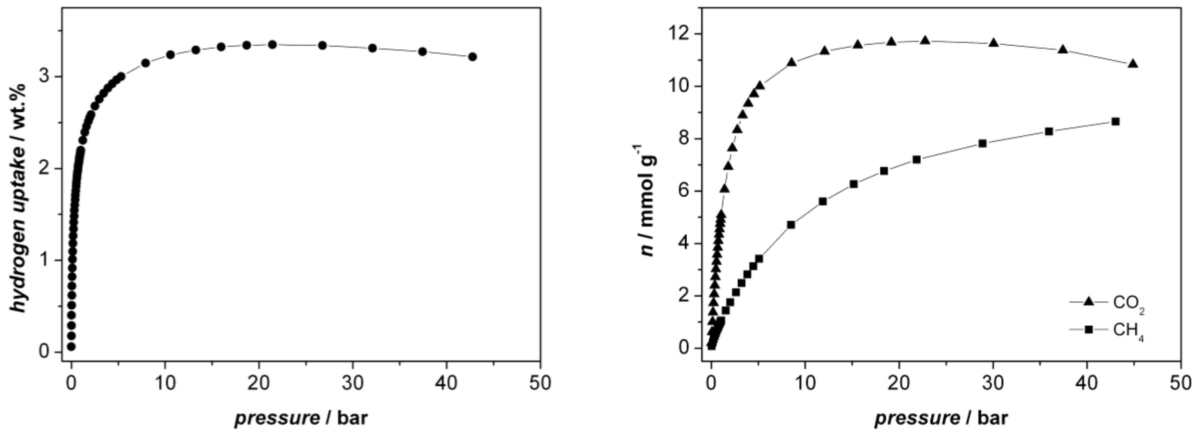


Figure S6: 40 bar H_2 sorption measurement at 77 K (left) and CO_2 and CH_4 adsorption measurements of $Cu_3(NH_2btc)_2$ at 298 K (right).

Characterisation of PSM on $Cu_3(NH_2btc)_2$

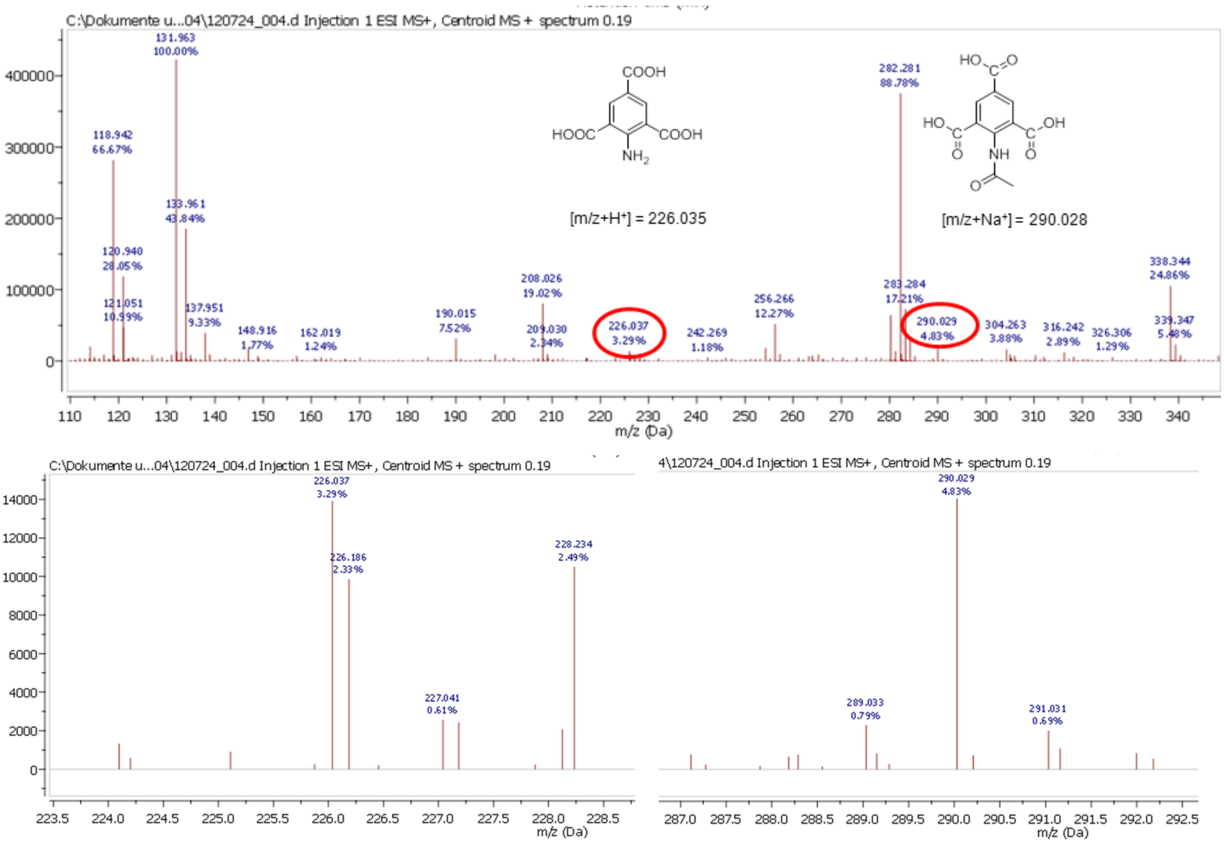


Figure S7: ESI-MS analysis shows the existence of unmodified linker as hydrogen adduct $[m/z + H^+] = 226.035$ and the modified linker as sodium adduct $[m/z + Na^+] = 290.029$. The relative intensity of the modified linker increases with increasing amount of acetic anhydride.

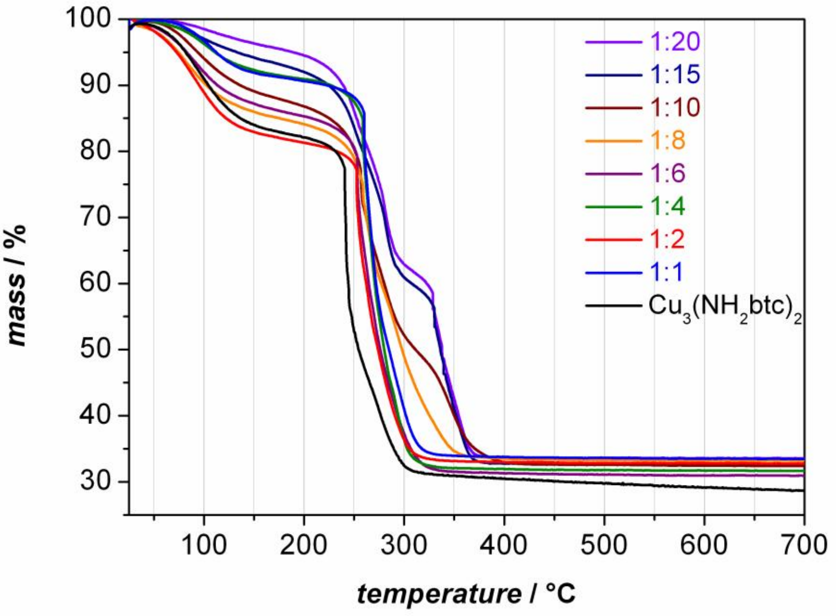


Figure S8: Thermogravimetric analysis of $Cu_2(NH_2btc)_2$ (black) and the modified samples (colored). The thermal stability of the modified samples slightly increases relative to the unmodified $Cu_3(NH_2btc)_2$.

Literature

[1] F. Micheel, W. Busse, *Chemische Berichte*, 1957, **90**, 2049-2053.

[2] Y. Li, G. Manickam, A. Ghoshal, P. Subramaniam, *Syntehtic Communications*, 2006, **36**, 925-928.

[3] CrysAlisPro, Version 1.171.35.19, Agilent Technologies Inc., **2011**.

[4] SHELXTL NT Version 5.1. Program for Solution and Refinement of Crystal Structures. University of Göttingen: Germany: G. M. Sheldrick, **1997**.

[5] Spek, A. L., J Appl Crystallogr **2003**, 36, 7-13