Electronic Supplementary Information

Synthesis and characterization of bimetallic metal-organic framework Cu-Ru-BTC with HKUST-1 structure

Meike A. Gotthardt[a], Roland Schoch[b], Silke Wolf[c], Matthias Bauer[b],* and Wolfgang Kleist[a,d],*

Author affiliations:

[a] Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), Engesserstr. 20, 76131 Karlsruhe, Germany.

[b] Department Chemie, Fakultät für Naturwissenschaften, Universität Paderborn, Warburgerstr. 100, 33098 Paderborn, Germany, tel.: +49 5251 605614, e-mail address: matthias.bauer@upb.de.

[c] Institute for Inorganic Chemistry, Karlsruhe Institute of Technology (KIT), Engesserstr. 15, 76131 Karlsruhe, Germany.

[d] Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany, tel.: +49 721 60847989, e-mail address: wolfgang.kleist@kit.edu.

1. Synthesis of $Cu_{2.75}Ru_{0.25}(BTC)_2*xH_2O$:

0.9352 g $Cu(NO_3)_2*3H_2O$ (3.87 mmol) and 0.2580 g $RuCl_3*xH_2O$ (38 w% Ru, 0.97 mmol) were dissolved at 60 °C in 25 mL ethanol. A solution of 0.4910 g benzene-1,3,5-tricarboxylic acid (2.34 mmol) in 25 mL *N,N*-dimethylformamide (DMF) was added and the reaction mixture was stirred under reflux for 24 h at 60 °C. After filtration the resulting material was washed with 5 x 25 mL DMF and 5 x 25 mL ethanol. The samples were dried over night at room temperature and then for three days at 130 °C in air atmosphere.

2. Synthesis of Cu-BTC

1.1690 g $Cu(NO_3)_2*3H_2O$ (4.48 mmol) were dissolved in 25 mL H_2O at 100 °C. A solution of 0.4910 g benzene-1,3,5-tricarboxylic acid (2.34 mmol) in 25 mL *N,N*-dimethylformamide (DMF) was added and the reaction mixture was stirred under reflux for 24 h at 100 °C. After filtration the resulting material was washed with 5 x 25 mL DMF and 5 x 25 mL H_2O. The samples were dried over night at room temperature and then for three days at 130 °C in air atmosphere.

3. Powder X-ray diffraction (PXRD):

The measurements were performed using a Bruker D8 Advance. The samples were analyzed in the range $2\,\Theta = 5 – 50°$ using Cu Kα radiation. The step width was $2\,\Theta = 0.0082°$ with a dwell time of 2 s.

4. Inductively coupled plasma optical emission spectrometry (ICP-OES):

To determine the metal content of the sample ICP-OES was carried out using an Agilent 725. Argon was used as carrier gas and to create the plasma. The sample was dissolved for 1 h in 5 mL nitric acid, 3 mL hydrochloric acid and 0.5 mL hydrogen peroxide using a 600 W microwave oven from Anton Parr (max. 240 °C and 60 bars). The results for Cu-Ru-BTC are shown in Table S1.

Table S1 Metal contents of Cu-Ru-BTC according to ICP-OES measurements.

	wt%	molar ratio
ruthenium	3.2	1
copper	23.0	11

5. Infrared spectroscopy (FT-IR):

IR data were acquired using a FT-IR spectrometer Vertex 70 from Bruker Optics equipped with a Golden Gate Single Reflection ATR sample cell from Specac. The data were collected from 4500 to 600 cm^{-1} and for each spectrum the arithmetic average of 400 measurements was taken. ATR-IR spectra of Cu-BTC, Cu-Ru-BTC and benzene-1,3,5-tricarboxylic acid are shown in Fig. S1.

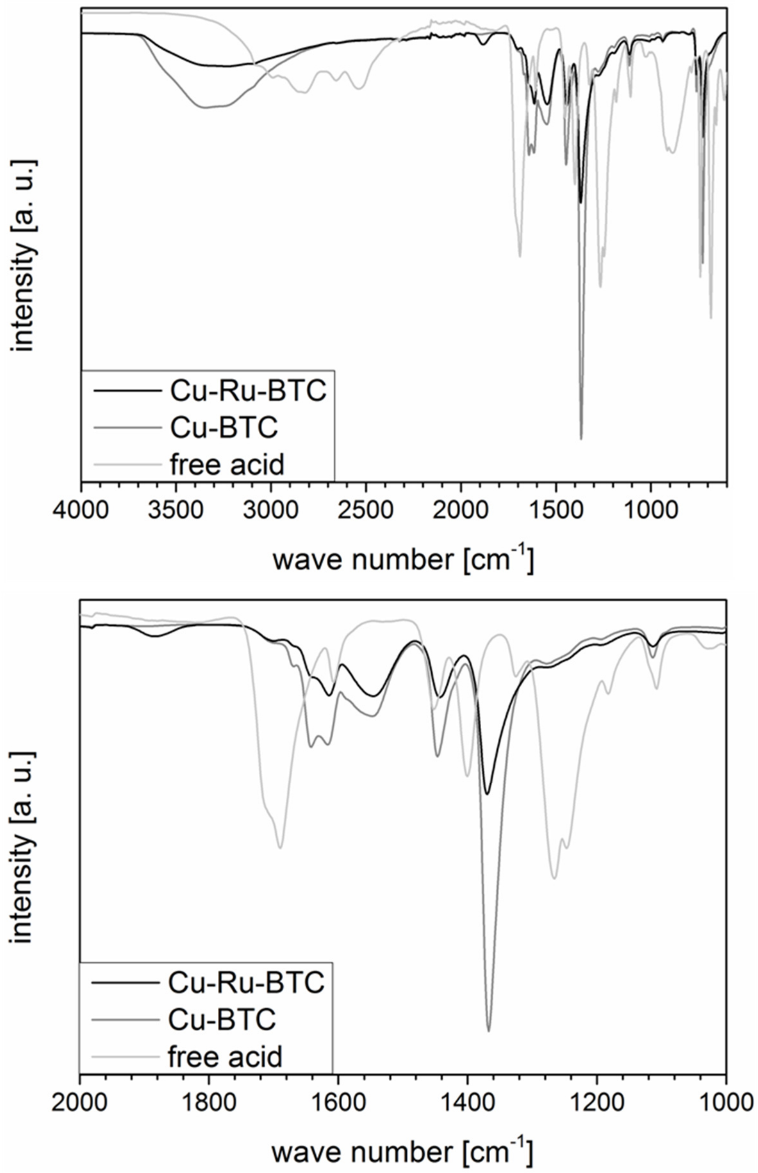

Fig. S1 ATR-IR spectra of Cu-Ru-BTC (black), Cu-BTC (dark grey) and benzene-1,3,5-tricarboxylic acid (light grey).

6. Nitrogen physisorption:

The samples were activated for 20 h at 130 °C under vacuum and analyzed using a Belsorp mini II from BEL Japan. Surface areas were determined using the BET and Langmuir method. Adsorption/desorption isotherms of Cu-BTC and Cu-Ru-BTC are shown in Fig. S2. Specific surface areas and micropore volumes are given in Table S2.

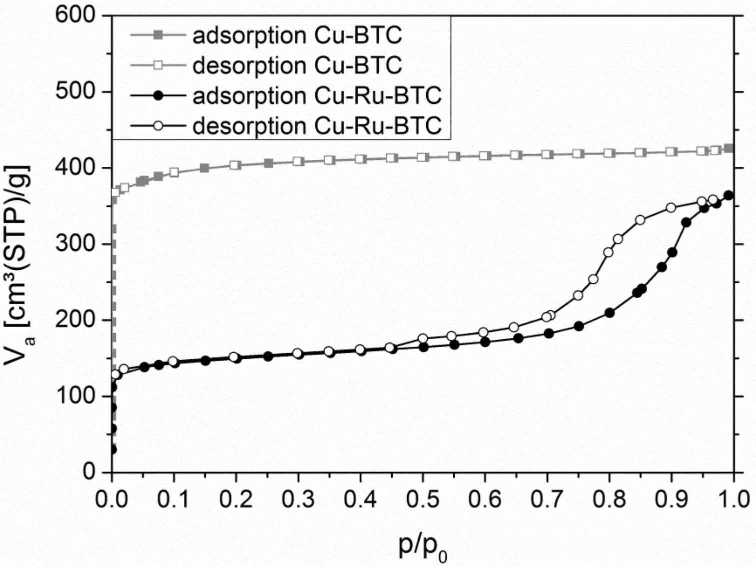

Fig. S2 Adsorption/desorption isotherms of Cu-Ru-BTC (black) and Cu-BTC (grey).

Table S2 Results of the nitrogen physisorption measurements of Cu-Ru-BTC and Cu-BTC.

sample	S_{BET} [m²/g]	$S_{Langmuir}$ [m²/g]	micropore volume [cm³/g]
Cu-Ru-BTC	570	710	0.18
Cu-BTC	1560	1850	0.60

7. Differential thermal analysis/thermogravimetry (DTA/TG)

Differential thermal analysis/thermogravimetry (DTA/TG) was performed with a NETZSCH STA 409C applying α-Al_2O_3 as crucible material and reference sample. The samples were heated under air flow from room temperature to 800 °C with a heating rate of 5 K/min.

8. X-ray absorption spectroscopy (XAS):

XAS experiments were performed at the "Spline" beamline BM25A at the ESRF (European Synchrotron Radiation Facility) in Grenoble, France, and at the XAS beamline at ANKA (Angströmquelle Karlsruhe) in Karlsruhe, Germany. For the measurements at the copper K-edge (8979 eV) a Si(111) double-crystal monochromator was used while at the Ru K-edge (22117 eV) a Si(311) double-crystal monochromator was applied. The maximum beam current at both synchrotrons was 200 mA with a ring energy of 2.5 GeV at ANKA and 6.0 GeV at ESRF. The solid samples for the copper K-edge were prepared as wafers using cellulose as a binder to avoid self-absorption effects in fluorescence mode at ambient temperature. The samples for the Ru K-edge were used undiluted due to the low ruthenium concentration. This caused strong self-absorption effects which were corrected using the X-ray absorption near edge structure (XANES) algorithm for fluorescence measurements of the program Athena[1].

For data evaluation a Victoreen-type polynomial was subtracted from the spectrum to remove the background.[2-5] Afterwards the first inflection point was taken as energy E_0. A piecewise polynomial was used to determine the smooth part of the spectrum. It was adjusted in a way that the low-R components of the resulting Fourier transform were minimal. The background subtracted spectrum was divided by its smoothed part and the photon energy was converted to photoelectron wave number *k*. For evaluation of the EXAFS spectra the resulting functions were weighted with k^3 and calculated with EXCURVE98 which works based on the EXAFS function and according to a formulation in terms of radial distribution functions[6, 7]:

$$\chi(k) = \sum_j S_0^2(k) F_j(k) \int P_j(r_j) \frac{e^{\frac{-2r_j}{\lambda}}}{kr_j^2} \sin\left[2kr_j + \delta_j(k)\right] dr_j$$

Due to the low ruthenium concentration and the therefore weak signal in the spectrum of the Ru K-edge Fourier filtering was necessary. The filtering was applied in distances from 1 Å to 3 Å (resulting spectrum shown in main paper Fig. 4). The corresponding untreated spectrum is shown in Fig. S3.

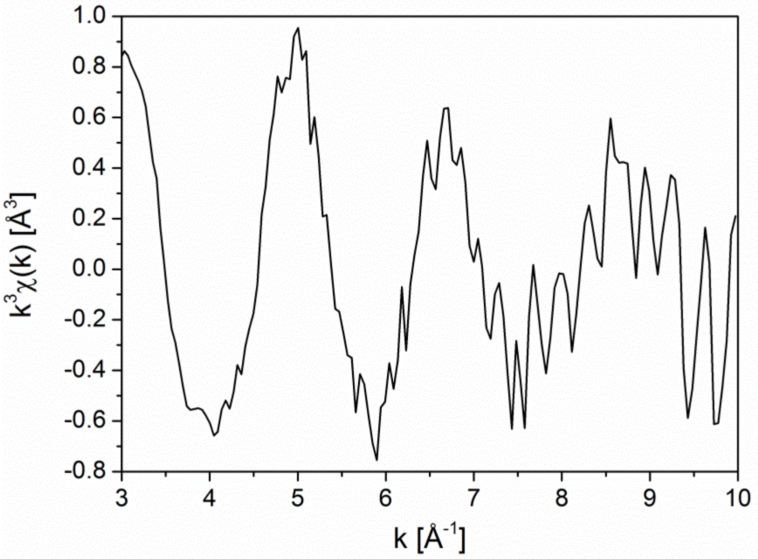

Fig. S3 EXAFS spectrum of Cu-Ru-BTC (Ru-edge) before Fourier filtering.

The number of independent points N_{ind} was calculated according to information theory to determine the degree of overdeterminacy[7]:

$$N_{ind} = \frac{2\Delta k \Delta R}{\pi}$$

Here, *Δk* describes the range in *k*-space used for data analysis and *ΔR* corresponds to the distance range in the Fourier filtering process. The results are given in Table S3:

Table S3 Used *k*-ranges, *R*-ranges and resulting number of independent points of Cu-Ru-BTC and Cu-BTC.

sample	Δk	ΔR	N_{ind}
Cu-Ru-BTC Cu-edge	11 (3 Å^{-1} – 14 Å^{-1})	4 (1 Å – 5 Å)	28.0
Cu-Ru-BTC Ru-edge	7 (3 Å^{-1} – 10 Å^{-1})	4 (1 Å – 5 Å)	17.8
Cu-BTC Cu-edge	10 (3 Å^{-1} – 13 Å^{-1})	4 (1 Å – 5 Å)	25.4

The quality of a fit was determined using two methods. The reduced χ^2_{red} considers the degree of overdeterminacy of the system and the number of fitted parameters *p*. It therefore allows a direct comparison of different models[8]:

$$\chi^2_{red} = \frac{(N_{ind}/N)}{N_{ind} - p} \sum_i \left(\frac{k_i^n}{\sum_j k_j^n \left| \chi_j^{exp}(k_j) \right|} \right)^2 (\chi^{exp}(k_i) - \chi^{theo}(k_i))^2$$

The R-factor, which represents the percentaged disagreement between experiment and adjusted function takes into account both systematic and random errors according to the equation[8]:

$$R = \sum_i \frac{k_i^n}{\sum_j k_j^n \left|\chi_j^{exp}(k_j)\right|} \left|\chi^{exp}(k_i) - \chi^{theo}(k_i)\right| \cdot 100\%$$

Literature

[1] B. Ravel and M. Newville, *J. Synchrotron Rad.* **2005**, *12*, 537-541.

[2] T. S. Ertel, H. Bertagnolli, S. Hückmann, U. Kolb and D. Peter, *Appl. Spectrosc.* **1992**, *46*, 690-698.

[3] M. Newville, *J. Synchrotron Rad.* **2001**, *8*, 322-324.

[4] M. Newville, P. Livins, Y. Yacoby, J. J. Rehr and E. A. Stern, *Phys. Rev. B* **1993**, *47*, 14126-14131.

[5] B. Ravel and M. Newville, *J. Synchrotron Rad.* **2005**, *12*, 537-541.

[6] N. Binsted and S. S. Hasnain, *J. Synchrotron. Radiat.* **1996**, *3*, 185-196.

[7] N. Binsted and F. Mosselmans, *EXCURV98 Manual*, Daresbury, UK.

[8] M. Bauer and H. Bertagnolli, *J. Phys. Chem. B* **2007**, *111*, 13756-13764.