Electronic supporting information

The introduction of functional side groups and the application of the mixed-linker concept in divalent MIL-53(Ni) materials

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1. Characterization of a Ni-ABDC material

A Ni-ABDC material was synthesized analogously to MIL-53(Ni), but terephthalic acid was substituted by 2-aminoterephthalic acid. Based on the powder X-ray diffraction pattern (see Fig. S1), the structure of the obtained crystalline Ni-ABDC material could not be resolved, but a literature report with a matching pattern was found, which could not provide an unambiguous structure determination.[1] ^{1}H-NMR spectra (see Fig. S2) of the digested Ni-ABDC material showed that only 2-aminoterephthalate was present and no PNO could be found. Additionally, the IR spectrum (see Fig. S3) suggested that the amine group was coordinated directly to nickel centers, since the two characteristic bands were redshifted by 200 cm^{-1} compared to pure 2-aminoterephthalic acid or MIL-53(Al)-NH_2 [2], which was interpreted differently by Guo *et al*.[1]

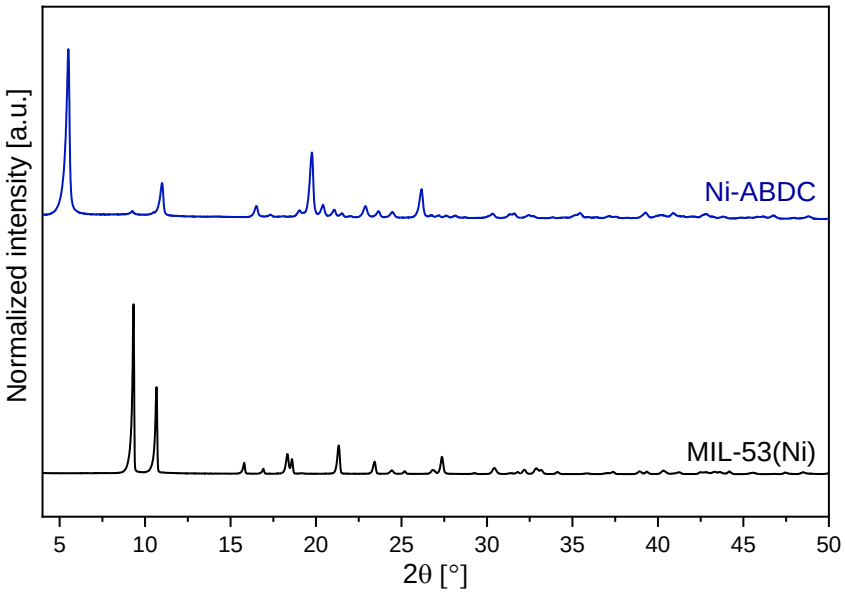

Fig. S1 Powder X-ray diffraction patterns of the Ni-ABDC material in comparison to MIL-53(Ni).

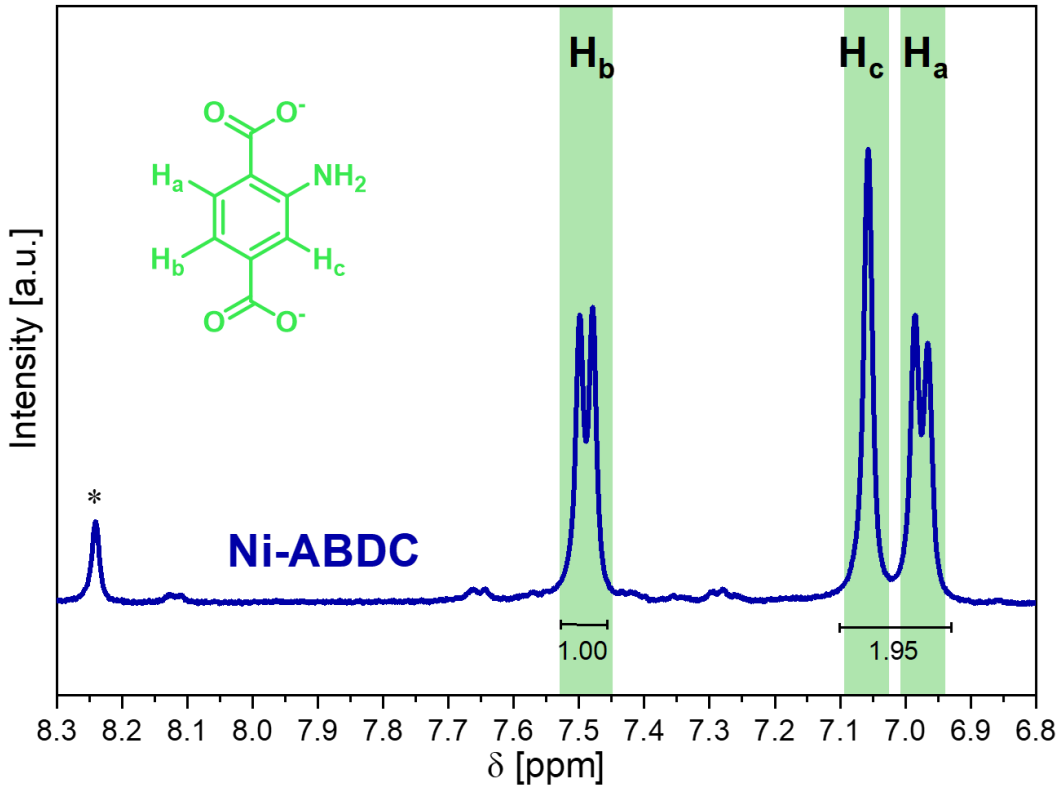

Fig. S2 ^{1}H-NMR spectrum of digested Ni-ABDC. * The signal at δ = 8.24 was assigned to formate, which was formed during synthesis through the decomposition of DMF.

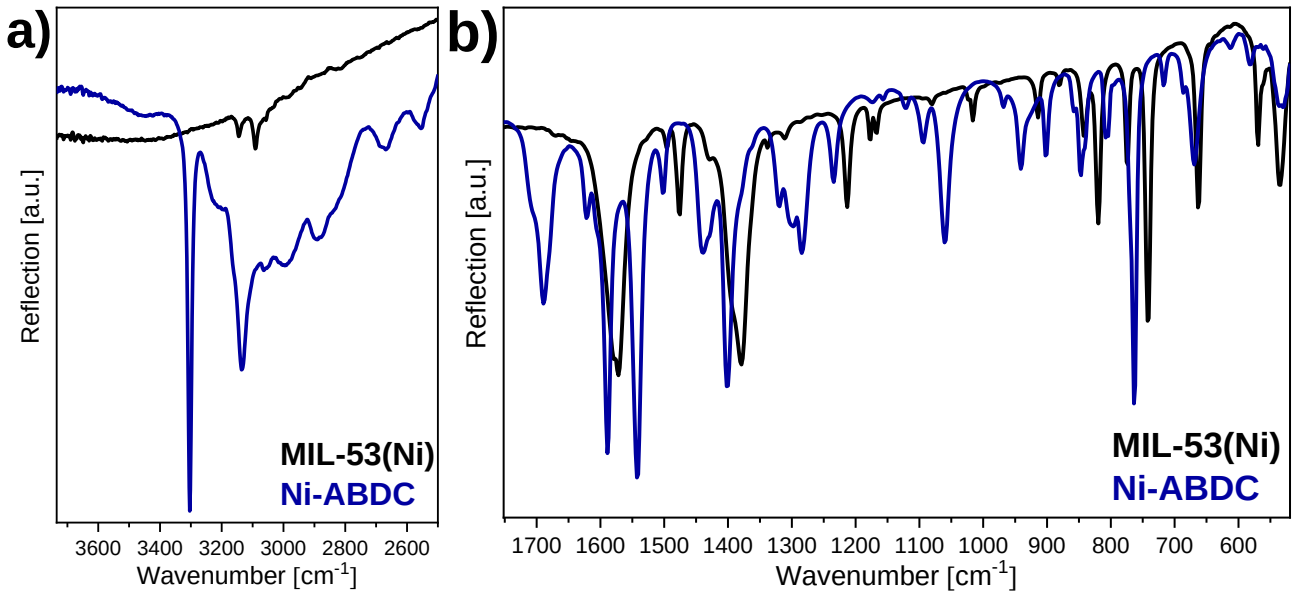

Fig. S3 ATR-IR spectrum of Ni-ABDC material in comparison to MIL-53(Ni), which show the region of amine band (a) and of carboxylate and C-H vibrations (b).

2. ^{1}H-NMR spectra

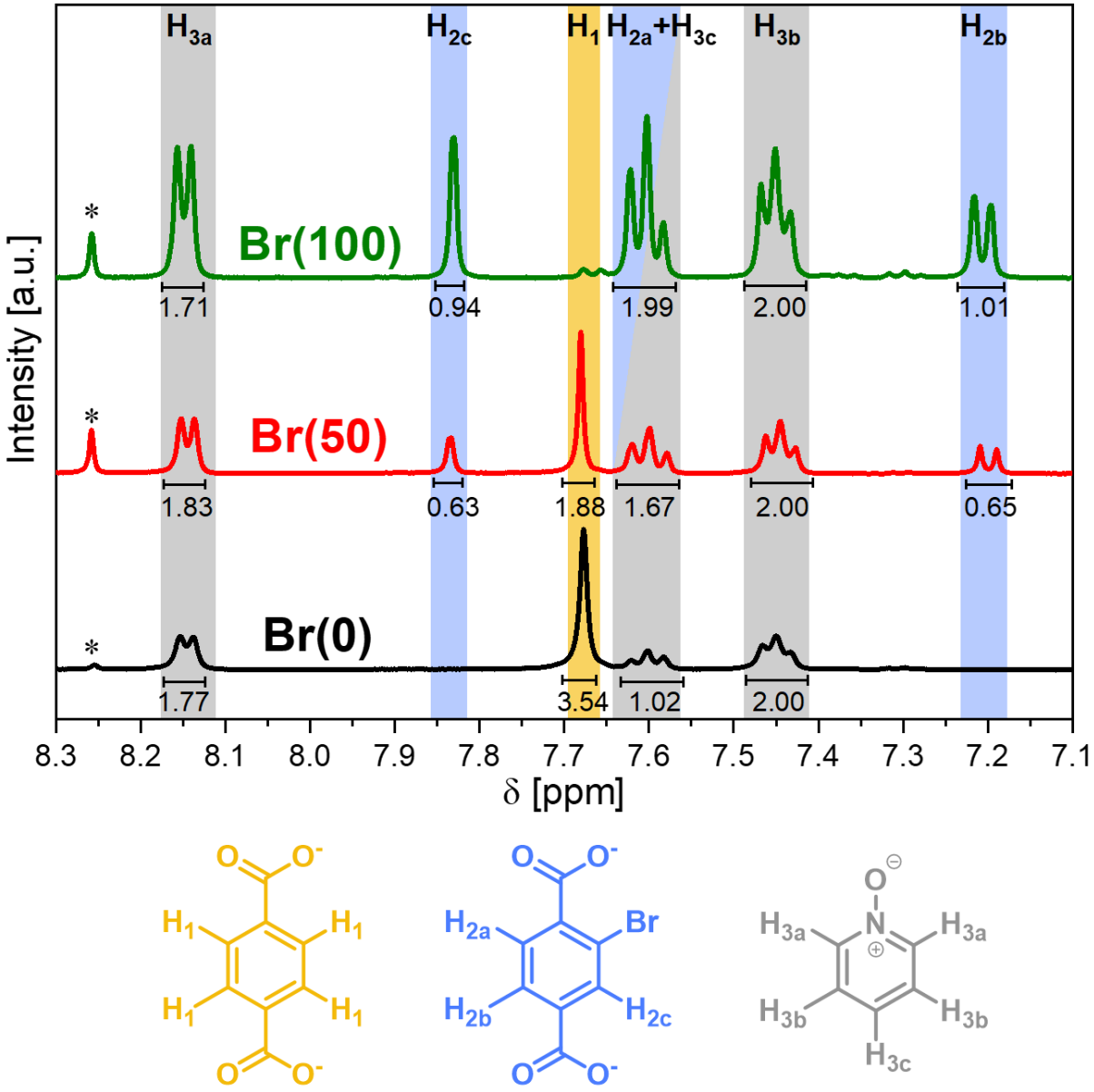

Fig. S4 ^{1}H-NMR spectra of digested materials; MIL-53(Ni), MIL-53(NI)-Br(50) and MIL-53(Ni)-Br(100). The peak close to δ = 8.14 had a significantly smaller integral than expected, because the corresponding protons were exchanged over time in the alkaline solution, which was used for the digestion of all materials. * The signal at δ = 8.25 was assigned to formate, which was formed during synthesis through the decomposition of DMF.

3. Refinement results

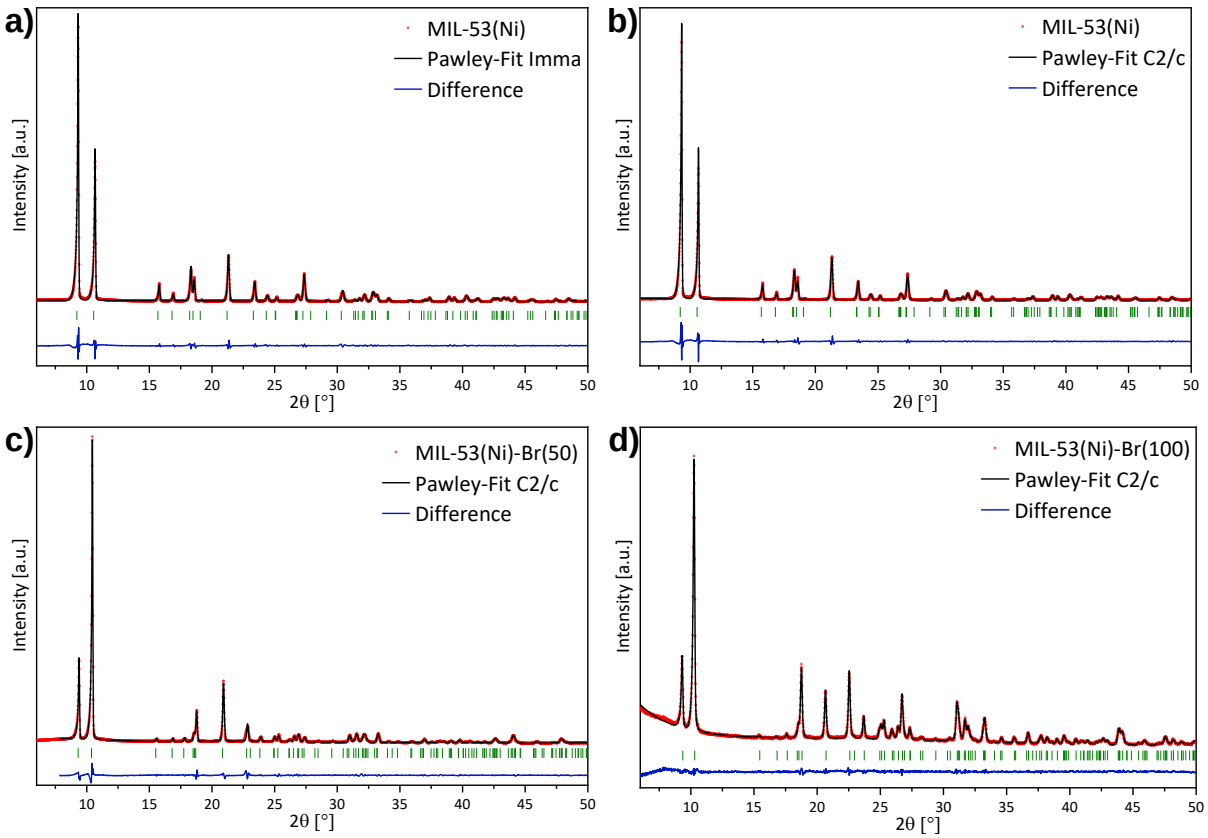

Fig. S5 Pawley refinement of MIL-53(Ni) using the space group *Imma* (a) and *C2/c* (b) and of MIL-53(Ni)-Br(X) (c) and MIL-53(Ni)-Br(X) (d) using the space group *C2/c*. The corresponding unit cell parameters of refinements are listed in Table 2 in the main manuscript.

4. Visualization of the (110) and the (200) planes

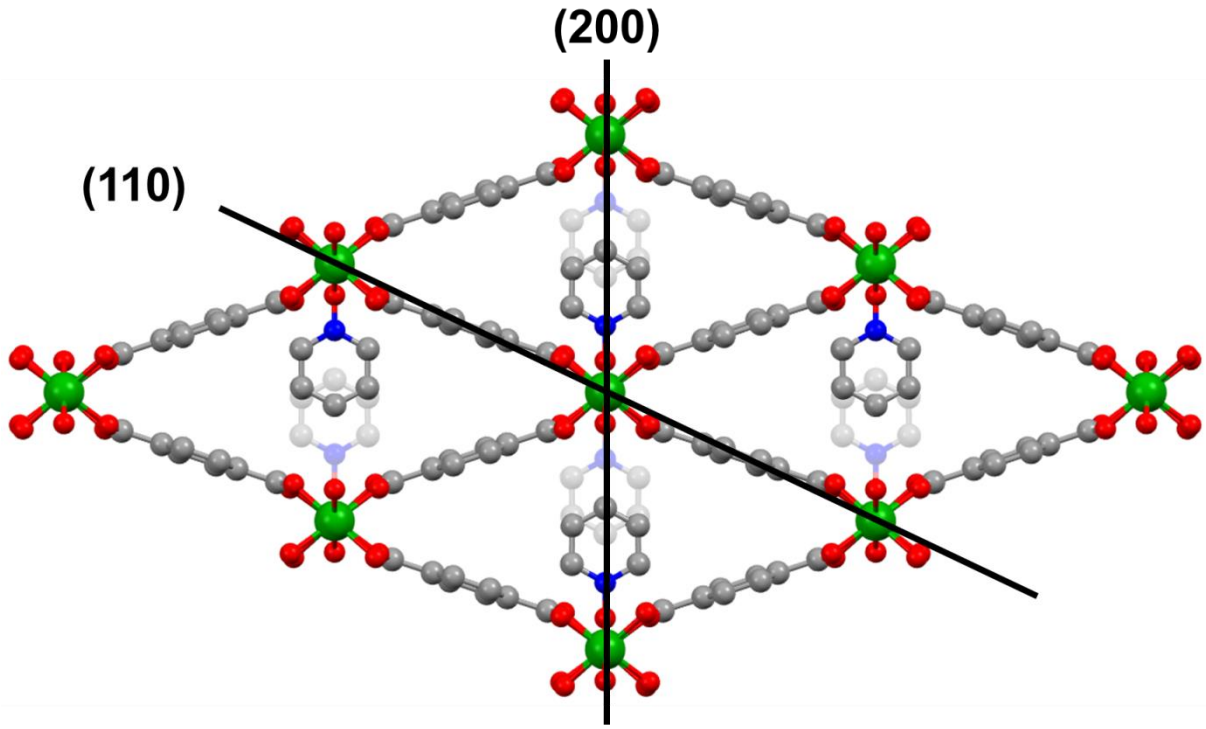

Fig. S6 Visualization of the (110) and (200) planes in the MIL-53(Ni) structure.

5. Calculation of pore dimensions

$$d_{long} = \sqrt{(\sin(180-\boldsymbol{\beta})*\mathbf{a})^2+\left(\sqrt{\mathbf{a}^2-(\sin(180-\boldsymbol{\beta})*\mathbf{a})^2}-\mathbf{c}\right)^2} \qquad \textbf{Equation (S1)}$$

$$d_{short} = \mathbf{b} \qquad \textbf{Equation (S2)}$$

with **a**, **b**, **c** and **β** unit cell parameters.

6. Supplementary EXAFS spectra

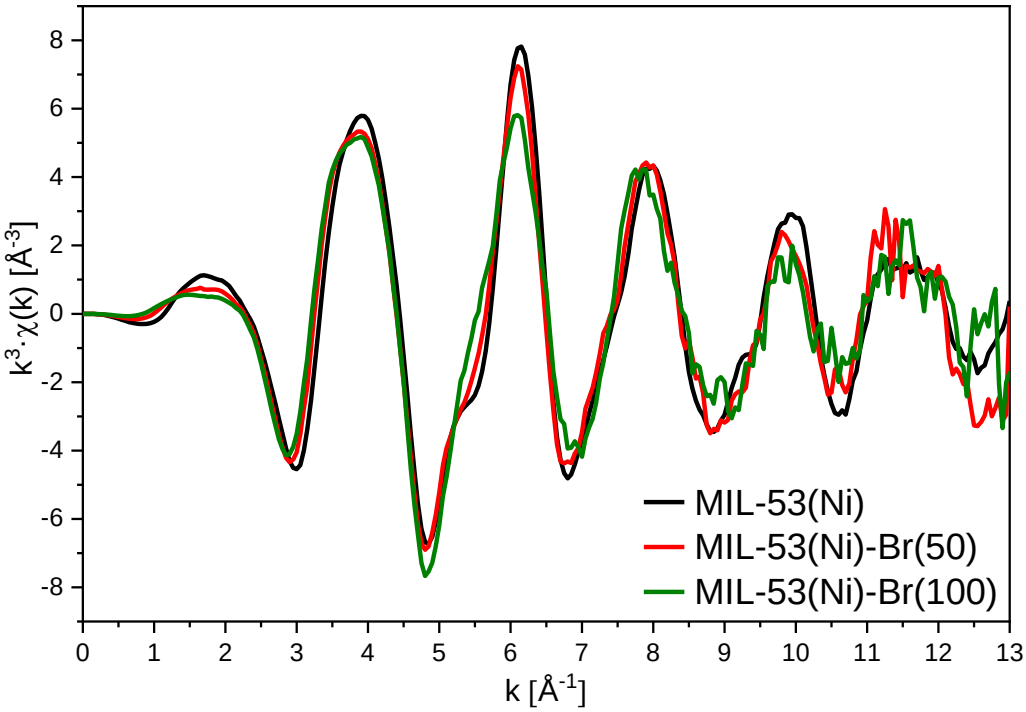

Fig. S7 Ni K-edge EXAFS spectra of MIL-53(Ni)-Br(X) materials.

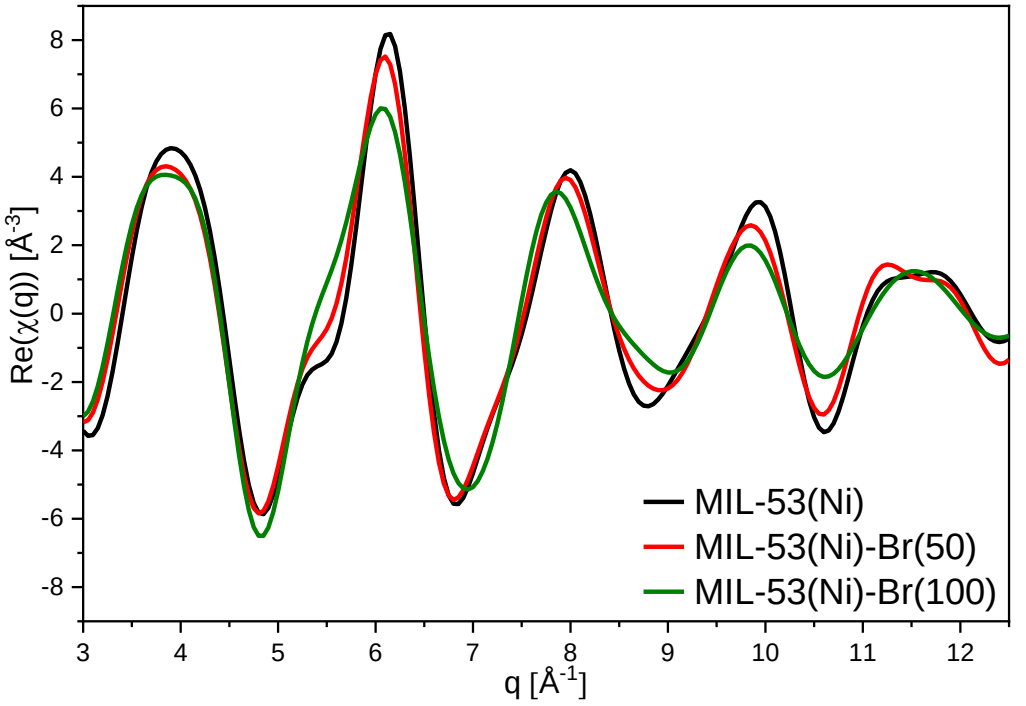

Fig. S8 Backtransformed Ni K-edge EXAFS spectra of MIL-53(Ni)-Br(X) materials (k-range: 3 - 12.5 $Å^{-1}$, R-range: 1.3 – 3.3 Å).

7. EXAFS fit results

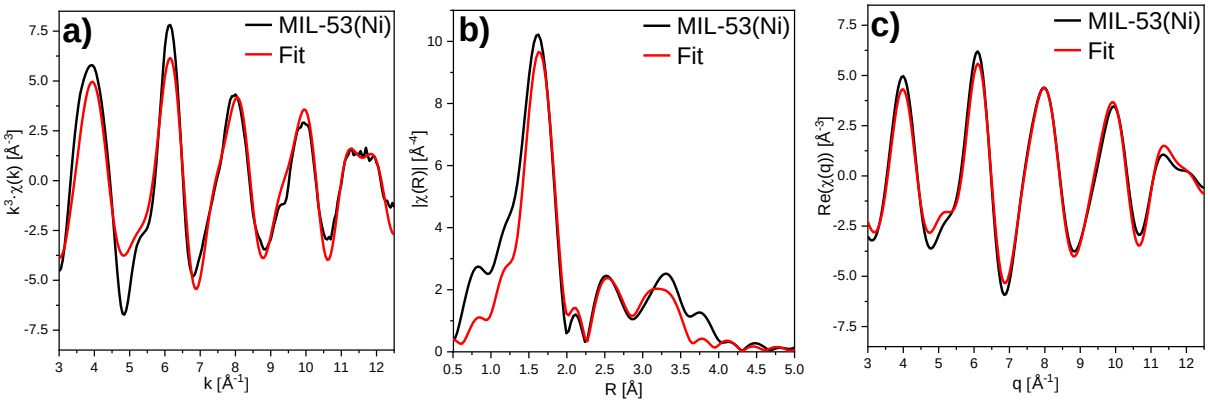

Fig. S9 Experimentally obtained EXAFS spectrum (a), Fourier-transformed EXAFS spectrum (b), the backtransformation thereof (c) and the corresponding best fit calculations of MIL-53(Ni).

Table S1 Best fit values for MIL-53(Ni).

Sample	Abs-Bs[a]	N(Bs)[b]	R(Abs-Bs)[c] [Å]	σ^2 [d] [Å²]
MIL-53(Ni)	Ni – O	6	2.04 ± 0.02	0.0043 ± 0.0007
Ni K-edge	Ni – C/N_{PNO}	6	3.00 ± 0.04	0.0079 ± 0.0037
	Ni – O_{IIa}	2	3.31 ± 0.08	0.0079 ± 0.0037
	Ni – O_{IIb}	2	3.38 ± 0.08	0.0079 ± 0.0037
	Ni – Ni	2	3.53 ± 0.04	0.0049 ± 0.0022
General fitting parameters	S_0^2 [e]= 0.810; ΔE_0 [f] = 3.35 ± 2.54 eV; χ^2_{red}[g] = 1687; R[h] = 0.026; N(path)[i] = 5; N(par)[j] = 8; k-range: 3 – 12.5; R-range: 1.3 - 3.3.			

[a] Abs = X-ray absorbing atom, Bs = backscattering atom. [b] Number of backscattering atoms. [c] Distance between absorbing and backscattering atom. [d] Debye-Waller factor. [e] Amplitude reduction factor. [f] Accounts for the shift of E_0 between theory and experiment. [g] Reduced χ^2 error (considers the number of independent points and number of varied parameters besides the error to the experiment). [h] Fit index.; [i] Total number of fitted paths including single and multiple scattering paths. [j] Number of free parameters used for the fit.

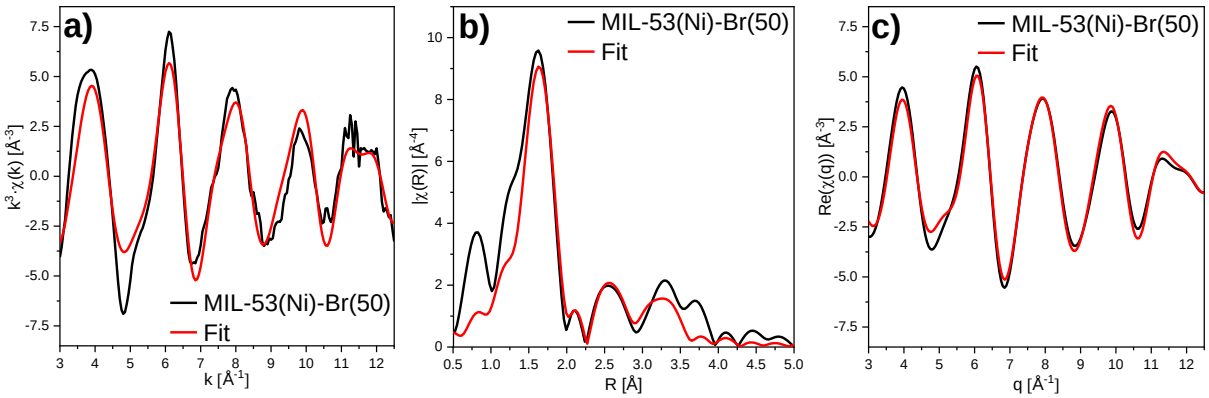

Fig. S10 Experimentally obtained EXAFS spectrum (a), Fourier-transformed EXAFS spectrum (b), the backtransformation thereof (c) and the corresponding best fit calculations of MIL-53(Ni)-Br(50).

Table S2 Best fit values for MIL-53(Ni)-Br(50).

Sample	Abs-Bs[a]	N(Bs)[b]	R(Abs-Bs)[c] [Å]	σ^2 [d] [Å²]
MIL-53(Ni)-Br(50)	Ni – O	6	2.05 ± 0.02	0.0046 ± 0.0008
Ni K-edge	Ni – C/N_{PNO}	6	3.01 ± 0.04	0.0077 ± 0.0037
	Ni – O_{IIa}	2	3.29 ± 0.08	0.0077 ± 0.0037
	Ni – O_{IIb}	2	3.35 ± 0.08	0.0077 ± 0.0037
	Ni – Ni	2	3.53 ± 0.04	0.0060 ± 0.0028
General fitting parameters	S_0^2 [e]= 0.810; ΔE_0 [f] = 2.05 ± 2.87 eV; χ^2_{red}[g] = 140; R[h] = 0.031; N(path)[i] = 5; N(par)[j] = 8; k-range: 3 – 12.5; R-range: 1.3 - 3.3.			

[a] Abs = X-ray absorbing atom, Bs = backscattering atom. [b] Number of backscattering atoms. [c] Distance between absorbing and backscattering atom. [d] Debye-Waller factor. [e] Amplitude reduction factor. [f] Accounts for the shift of E_0 between theory and experiment. [g] Reduced χ^2 error (considers the number of independent points and number of varied parameters besides the error to the experiment). [h] Fit index.; [i] Total number of fitted paths including single and multiple scattering paths. [j] Number of free parameters used for the fit.

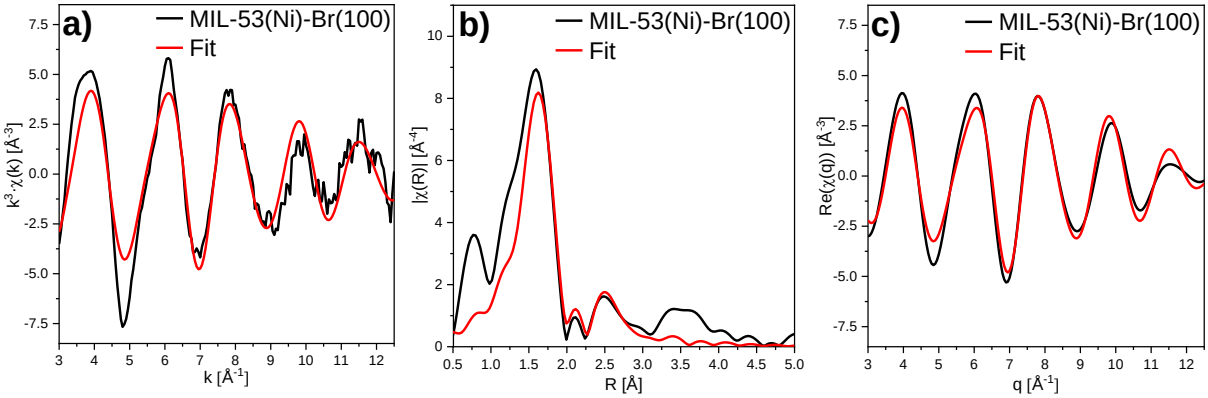

Fig. S11 Experimentally obtained EXAFS spectrum (a), Fourier-transformed EXAFS spectrum (b), the backtransformation thereof (c) and the corresponding best fit calculations with nickel neighbors of MIL-53(Ni)-Br-(100).

Table S3 Best fit values for MIL-53(Ni)-Br(100) with nickel neighbors.

Sample	Abs-Bs[a]	N(Bs)[b]	R(Abs-Bs)[c] [Å]	σ^2 [d] [Å²]
MIL-53(Ni)-Br(100)	Ni – O	6	2.05 ± 0.02	0.0054 ± 0.0011
Ni K-edge	Ni – C/N_{PNO}	6	2.98 ± 0.07	0.0103 ± 0.0086
With Ni neighbors	Ni – O_{IIa}	2	3.22 ± 0.13	0.0103 ± 0.0086
	Ni – O_{IIb}	2	3.28 ± 0.13	0.0103 ± 0.0086
	Ni – Ni	2	3.45 ± 0.15	0.0168 ± 0.0225
General fitting parameters	S_0^2 [e]= 0.810; ΔE_0 [f] = 0.85 ± 4.02 eV; χ^2_{red}[g] = 159; R[h] = 0.055; N(path)[i] = 5; N(par)[j] = 8; k-range: 3 – 12.5; R-range: 1.3 - 3.3.			

[a] Abs = X-ray absorbing atom, Bs = backscattering atom. [b] Number of backscattering atoms. [c] Distance between absorbing and backscattering atom. [d] Debye-Waller factor. [e] Amplitude reduction factor. [f] Accounts for the shift of E_0 between theory and experiment. [g] Reduced χ^2 error (considers the number of independent points and number of varied parameters besides the error to the experiment). [h] Fit index.; [i] Total number of fitted paths including single and multiple scattering paths. [j] Number of free parameters used for the fit.

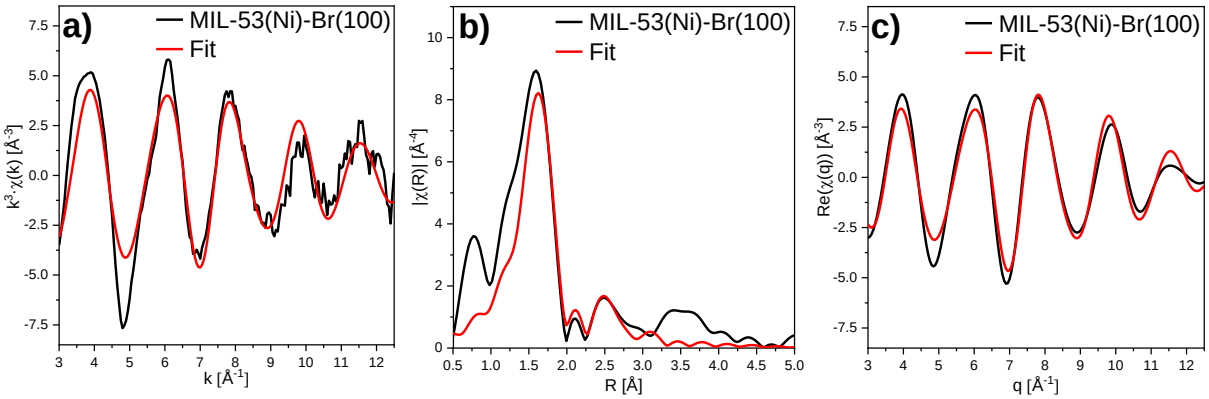

Fig. S12 Experimentally obtained EXAFS spectrum (a), Fourier-transformed EXAFS spectrum (b), the backtransformation thereof (c) and the corresponding best fit calculations without nickel neighbors of MIL-53(Ni)-Br-(100).

Table S4 Best fit values for MIL-53(Ni)-Br(100) without nickel neighbors.

Sample	Abs-Bs[a]	N(Bs)[b]	R(Abs-Bs)[c] [Å]	σ^2 [d] [Å²]
MIL-53(Ni)-Br(100)	Ni – O	6	2.05 ± 0.02	0.0054 ± 0.0009
Ni K-edge	Ni – C/N_{PNO}	6	2.98 ± 0.06	0.0115 ± 0.0064
Without Ni neighbors	Ni – O_{IIa}	2	3.25 ± 0.09	0.0115 ± 0.0064
	Ni – O_{IIb}	2	3.31 ± 0.09	0.0115 ± 0.0064
General fitting parameters	S_0^2 [e]= 0.810; ΔE_0 [f] = 0.87 ± 3.21 eV; χ^2_{red}[g] = 109; R[h] = 0.057; N(path)[i] = 4; N(par)[j] = 6; k-range: 3 – 12.5; R-range: 1.3 - 3.3.			

[a] Abs = X-ray absorbing atom, Bs = backscattering atom. [b] Number of backscattering atoms. [c] Distance between absorbing and backscattering atom. [d] Debye-Waller factor. [e] Amplitude reduction factor. [f] Accounts for the shift of E_0 between theory and experiment. [g] Reduced χ^2 error (considers the number of independent points and number of varied parameters besides the error to the experiment). [h] Fit index.; [i] Total number of fitted paths including single and multiple scattering paths. [j] Number of free parameters used for the fit.

8. References

1 H. Guo, Z. Zheng, Y. Zhang, H. Lin and Q. Xu, *Sens. Actuators, B*, 2017, **248**, 430–436.

2 M. A. Gotthardt, R. Schoch, T. S. Brunner, M. Bauer and W. Kleist, *ChemPlusChem*, 2015, **80**, 188–195.