Electronic Supporting Information

Tuning functional sites and thermal stability of mixed-linker MOFs based on MIL-53(Al)

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Experimental Details

General

All chemicals were used without further purification or drying. *N,N*-dimethylformamide (DMF, > 99.8%), aluminum nitrate nonahydrate ($Al(NO_3)_3 \times 9H_2O$, > 98.0%) and benzene-1,4-dicarboxylate (H_2BDC, > 99.0%) were purchased from Fluka. 2-aminobenzene-1,4-dicarboxylate (H_2ABDC, > 99+%) was purchased from Acros Organics.

Characterization of materials

Powder X-ray diffraction patterns were recorded on a Siemens D5000 diffractometer equipped with a Ni filter using Cu K_α radiation. Measurements were performed in the 2Θ range between 5 and 55° with a step size of 0.01° and a step time of 2 seconds. Peak positions were adjusted using a copper plate (Cu (111) peak at 43.3°) as a reference.

IR spectra have been recorded on a Bruker Vertex 70 equipped with a MCT detector cooled with liquid nitrogen. The spectra have been recorded in the range between 4000 and 400 cm^{-1} with a resolution of 2 cm^{-1} in the ATR mode. 500 scans have been collected for each sample.

^{13}C CP MAS NMR investigations were carried out on a Bruker Advance 500 spectrometer at resonance frequency of 125.758 MHz with a 4 mm Bruker MAS probe at a sample spinning rate of 13-14 kHz. Spectra were recorded after an excitation with a $\pi/2$ pulse with the contact time of 5 ms and with a repetition time of 2 s. The applied settings of the ^{13}C CP MAS NMR allow for the monitoring of the relative changes caused by the different BDC / ABDC ratios.

Thermal analysis was carried out on a Netzsch STA 409 thermal analyzer equipped with a gas pulse device, which enables the injection of a certain amount of gas mixtures into the system. The experiments could be done under isothermal or non-isothermal conditions. The heating rates were generally in the range of 5-10 K min^{-1}. The thermal stability of the MOFs was examined in an atmosphere of 20 vol% O_2 in He, using a total gas flow of 50 cm^3 min^{-1}.

Synthesis of MIL-53 and NH_2-MIL-53

In a typical experiment aluminum nitrate nonahydrate (2.0 g, 5.33 mmol, 1 eq.) was dissolved at RT in deionized water (23 cm^3) in a teflon vessel. H_2BDC (949 mg, 5.33 mmol, 1 eq.) was added to the resulting colorless solution and the suspension was stirred 5 minutes at r.t. The teflon inlet was placed in a stainless steel autoclave, sealed and left in a oven for 5 hours at 150 °C. The resulting colorless precipitate was filtered of and washed with water (100 cm^3). The material was dried for 3.5 h at 130 °C yielding a colorless product. The raw material was then washed in boiling DMF for 2 h. The purified product was obtained after filtration and drying in a vacuum oven at 130°C.

The isoreticular NH_2-MIL-53 was synthesized according to the above described procedure by using H_2ABDC (966 mg, 5.33 mmol. 1 eq.) instead of H_2BDC. The resulting yellow precipitate was treated analogous to the pure MIL-53.

Synthesis of mixed linker MIL-53

A series of isoreticular metal organic framework was synthesized by using mixtures of the two linker molecules in the desired ratio. By variation of the ratio of H_2ABDC and H_2BDC one could obtain materials with different degrees of substitution. In this work materials with 0, 10, 50, 90 and 100 percent ABDC have been synthesized. The color of the ABDC substituted material was yellow, independent of the degree of substitution.

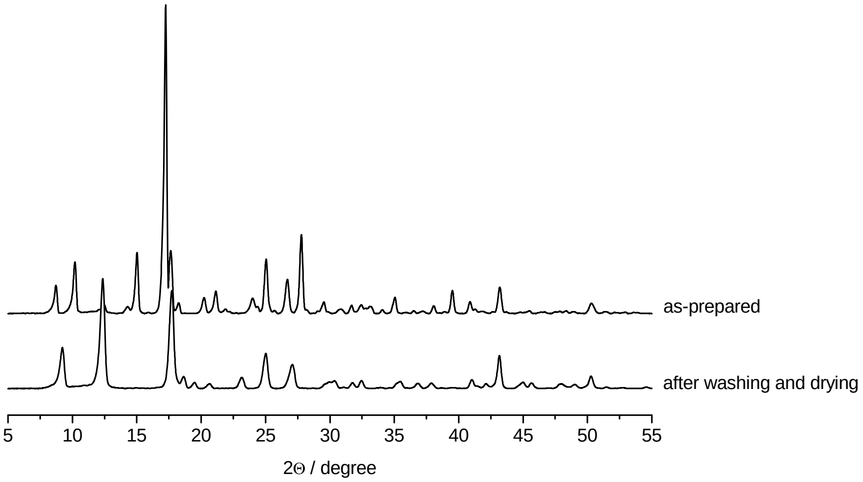

Fig. S1 XRD powder diffraction pattern of the MIXMOF containing 10 % ABDC before (top) and after removal of residual acid molecules. A typical breathing effect is observed upon exchange of the acid molecules by water which is adsorbed from the air after drying.

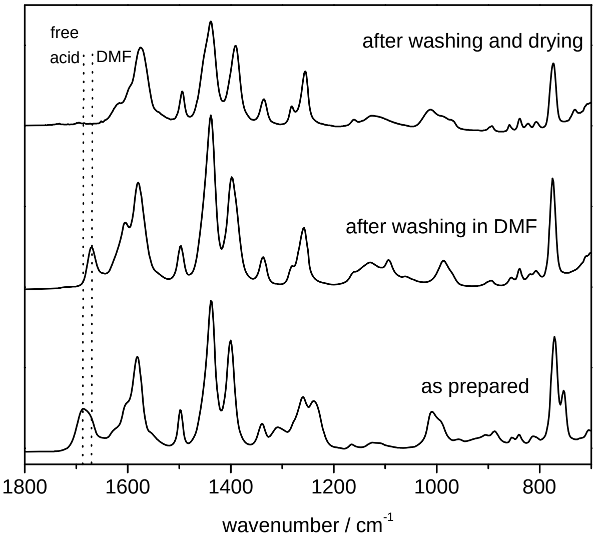

Fig. S2 IR spectra of the sample NH_2-MIL-53(Al) (100 % ABDC) as-prepared (bottom), after washing in DMF (middle) and after washing and drying (top). The dotted lines show the position of the C=O vibration of the free acid and DMF, respectively.

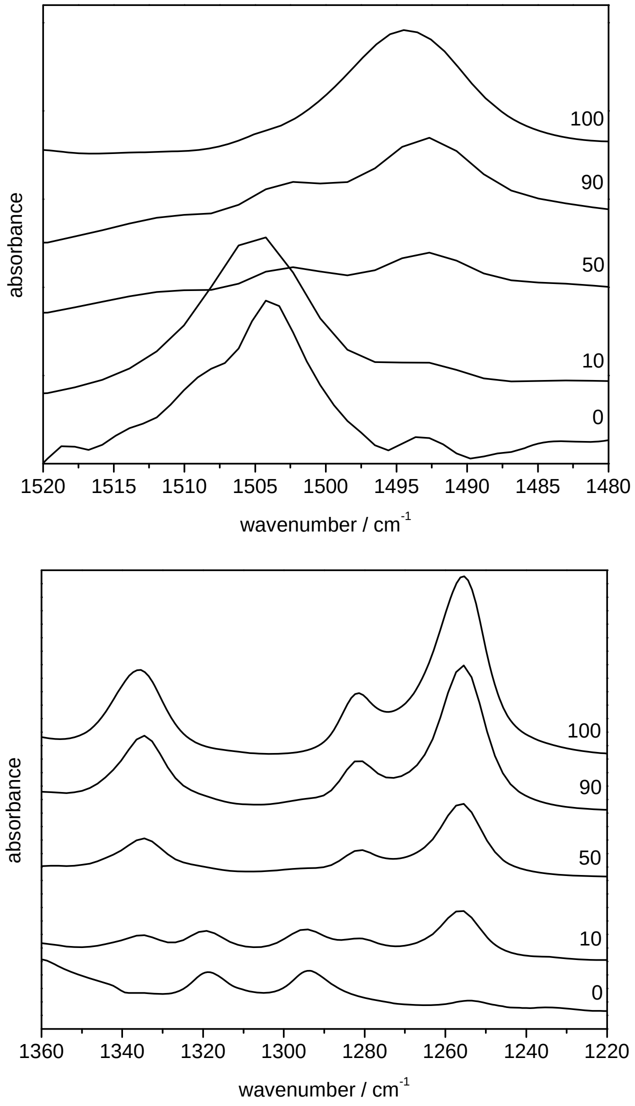

Fig. S3 ATR-IR spectra of the MIXMOFs (0 – 100 % ABDC); regions from 1520 to 1480 cm^{-1} (top) and 1360 – 1220 cm^{-1}. Bands from BDC and ABDC appear at different wavenumbers due to the different substitution pattern at the aromatic ring. The intensity of the corresponding bands is dependent on the ABDC/BDC ratio in the MIXMOFs.