

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

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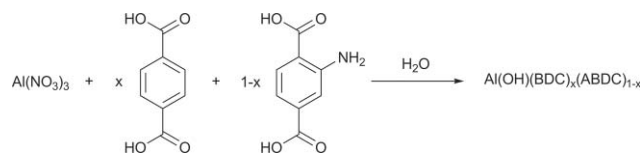
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The MIXMOF concept has been applied to the metal-organic framework compound MIL-53(Al). The random incorporation of two different linker molecules (benzene-1,4-dicarboxylate and 2-aminobenzene-1,4-dicarboxylate) in the framework structure and its influence on thermal stability were proven using several complementary techniques (XRD, ATR-IR, MAS-NMR and TG).

Metal-organic frameworks (MOFs) represent an interesting class of materials for various applications because of their unique properties.¹⁻⁴ Besides their huge specific surface areas and pore volumes, the ordered crystalline structure of this class of materials gave rise to applications of MOFs in gas storage and separation as well as in sensor techniques and catalysis.⁵ The nearly unlimited number of possible combinations of metal units and linking organic molecules allows for the design of various structural motifs with uniform and highly dispersed active sites which are important for adsorption processes or catalytic transformations. The most important strategies in the field of MOF catalysis include: (i) the immobilization of active catalytic species (nanoparticles or clusters) in the pores of the material,⁶⁻⁸ (ii) catalysis at coordinatively unsaturated framework metal centers,^{9,10} and (iii) catalytically active side groups at the organic linker molecule. In the latter case, the initial functionalities of the linker molecule (e.g. basic NH₂ groups of 2-aminobenzene-1,4-dicarboxylate) can act as the active centers themselves¹¹ or they can be further modified by post-synthetic covalent reactions leading to additional organic moieties.¹²⁻¹⁴ Furthermore, they can act as “surface ligands” for the immobilization of catalytically active transition metal complexes, thus representing a heterogeneous analog to homogeneous catalysts.^{15,16} While the strategies mentioned above focus, in general, on a stoichiometric or quantitative functionalization at all organic linker molecules (Scheme 1), it might be reasonable to tune the number and distribution of these active sites by using mixtures of two types of organic linker molecules. This MIXMOF concept, where one of the two linkers is only used for building the framework structure while the other is providing additional functional side group(s), has recently been demonstrated for MOFs based on the structures of MOF-5¹⁷⁻²⁰ and MIL-101(Cr).²¹

Here, we present the transfer of the MIXMOF concept to MIL-53(Al). Based on the known materials of this structure bearing



Scheme 1

exclusively benzene-1,4-dicarboxylate (BDC, MIL-53(Al))²²⁻²⁴ and 2-aminobenzene-1,4-dicarboxylate (ABDC, MIL-53-NH₂(Al))¹² we have synthesized a series of mixed-linker MOFs in which the amount of amine groups can be controlled by choosing the ratio of the two organic molecules. Since the structures of both ligand-pure frameworks are isorecticular (*i.e.* forming the same network), the replacement of one linker by another should be possible without changing the framework structure. The synthesized MIXMOFs have the molecular formula Al(OH)(BDC)_{1-x}(ABDC)_x with $x = 0.1; 0.5; 0.9$.

The synthesis of an isorecticular MIL-53 framework with randomly distributed organic linker molecules was done under hydrothermal conditions based on the reaction conditions for the pure frameworks. For the MIXMOFs 10%, 50% and 90%, respectively, of BDC were replaced by ABDC. The color of the material changes from colorless for the pure MIL-53 to yellow upon admixing of 2-aminobenzene-1,4-dicarboxylate.

The as-prepared materials contain residual acid molecules (H₂BDC and H₂ABDC) sitting in the pores of the material. Removal of these unreacted molecules is necessary to obtain a high surface area material with accessible pores. While free H₂BDC could be removed from MIL-53 by calcination,²² the stronger interactions of the NH₂ groups with the framework make a thermal removal of these species impossible without destroying the framework.¹² Therefore the MIXMOFs have been treated with boiling *N,N*-dimethylformamide (DMF) to dissolve the remaining, unreacted acid molecules leading to a porous structure. After drying of the powder to remove the solvent, water is adsorbed from air. Upon the exchange of the guest molecules the framework exhibits breathing behavior,²² which is clearly visible in the diffraction pattern of the washed sample compared to the as-prepared one (Fig. S1, Supporting Information†).

Besides monitoring these structural changes by XRD, IR spectroscopy was applied to ensure the complete removal of the free acid molecules (see Fig. S2, Supporting Information†). The signal at 1686 cm⁻¹, corresponding to the C=O stretching mode of the carboxyl moiety of free acid molecules, has disappeared after the treatment in DMF and a new band at 1670 cm⁻¹ is visible due to the C=O vibration of DMF which can be removed by subsequent drying.

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To prove the random incorporation of both linkers into the framework, powder X-ray diffraction patterns of the activated materials have been recorded. In Fig. 1 the diffraction pattern of the samples in the 2θ range between 5 and 55° (top) as well as 8 and 13° (bottom) are shown. The diffraction patterns of the materials look similar which indicates an isorecticular structure for all MIXMOFs presented here. Since the lattice parameters of MIL-53(Al) ($a = 19.513(2)$ Å, $b = 7.612(1)$ Å, $c = 6.576(1)$ Å) and MIL-53-NH₂(Al) ($a = 19.722(7)$ Å, $b = 7.692(3)$ Å, $c = 6.578(4)$ Å) differ only slightly, one would expect a small shift of the signals to lower 2θ with increasing content of ABDC in accordance to Vegard's law. This is true for the materials here. The first peak is shifted from 9.37 for the MIL-53 to 9.19 for the MIL-53-NH₂ which is in agreement with the larger lattice parameters of the latter. Moreover none of the peaks is split or shows a shoulder as one would expect for a physical mixture of two different MOFs, where two phases are present. Both observations confirm that a homogeneously mixed framework was prepared.

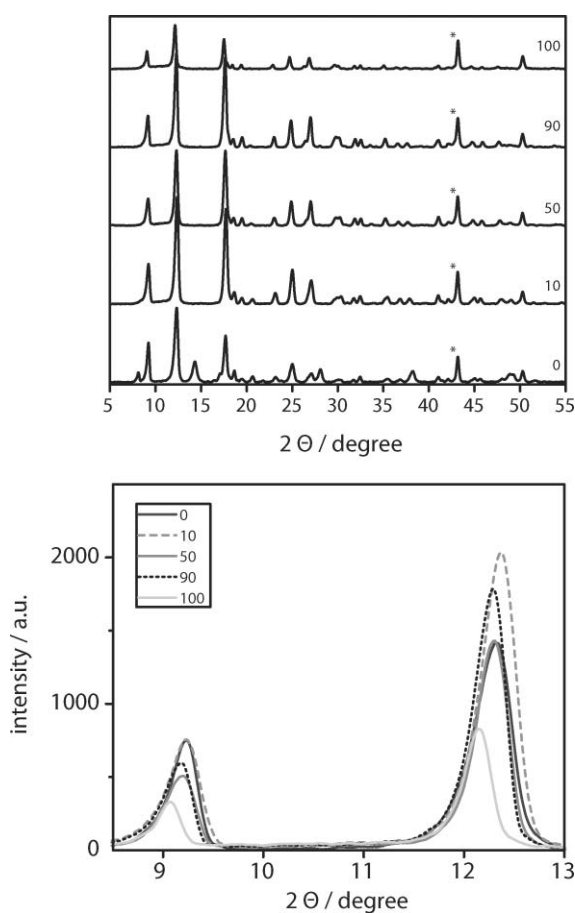


Fig. 1 XRD spectra of the MIXMOFs (0-100% ABDC) in the range between 5 and 55° (top); section of the spectra showing the shift of the signals with change of composition (bottom); the asterisk indicates the Cu (111) peak from the Cu reference.

The increasing degree of substitution of BDC by ABDC within the series has been proven using ATR-IR spectroscopy (Fig. 2 and S3, Supporting Information†). Four regions have been chosen to

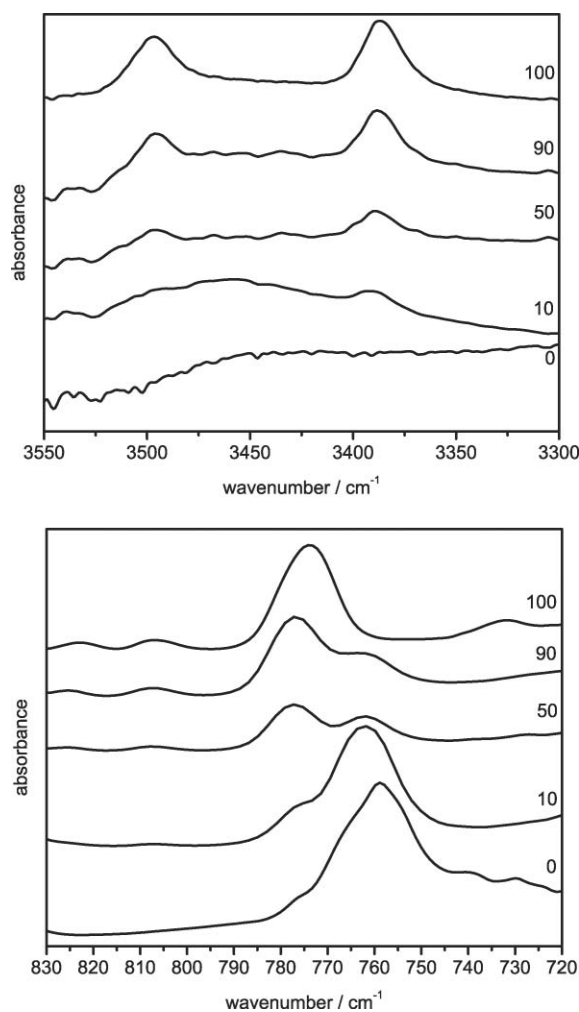


Fig. 2 ATR-IR spectra of the MIXMOFs (0-100% ABDC); regions of N–H stretch (3550 – 3300 cm⁻¹, top) and aromatic C–H deformation vibration (830 – 720 cm⁻¹, bottom).

exemplify the stepwise substitution of BDC by ABDC. In the region between 3550 cm⁻¹ and 3300 cm⁻¹ the signals from the symmetric and antisymmetric N–H stretching vibration of the amine are shown. The intensity of the two bands at 3498 cm⁻¹ and 3384 cm⁻¹ increases with increasing amount of ABDC (Fig. 2, top). In addition, a strong change is observed in the region of the aromatic deformation vibrations due to the different substitution patterns of the aromatic ring (Fig. 2, bottom). The intensity of the band located at 759 cm⁻¹ (from BDC) is decreasing with increasing substitution while the band at 774 cm⁻¹ (from ABDC) increases. A similar behavior is seen in the regions from 1520 to 1480 cm⁻¹ and from 1360 cm⁻¹ to 1220 cm⁻¹ (see Fig. S3, Supporting Information†).

Since the activated materials do not contain free acid, it was possible to monitor the incorporation of the two linker materials also by solid state NMR. In Fig. 3 the solid-state CP ¹³C spectra of the materials are shown. For the pure MIL-53(Al) three signals could be found, which correspond to the two carboxyl carbon atoms (174.5 ppm), the two quaternary carbon atoms of the phenyl ring (136.1 ppm) and the four remaining carbon atoms of the phenyl ring (129.7 ppm), respectively. With increasing substitution

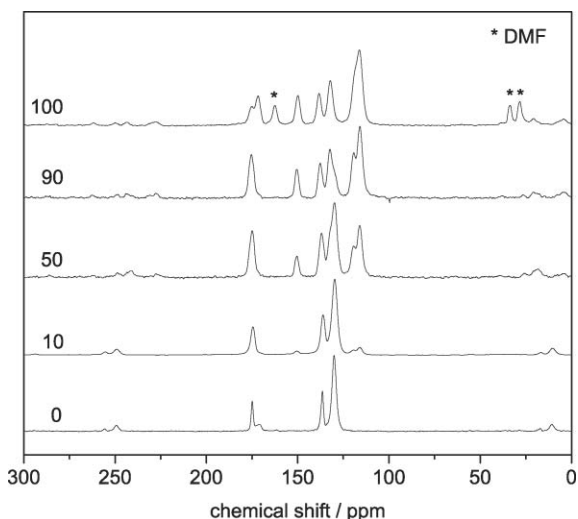


Fig. 3 ^{13}C CP MAS-NMR spectra of the MIXMOFs (0-100% ABDC); note that the reference sample MIL-53-NH₂(Al) (100% ABDC) was not completely dried and shows in addition signals from the solvent (DMF).

of BDC by ABDC new signals become visible. The broad signal at 175.0 can be assigned again to the two carboxyl carbon atoms. The new signal at 149.9 corresponds to the C_{phenyl}-NH₂ atom while the three signals between 138.3 and 116.3 are attributable to the five remaining non-equivalent carbon atoms of the substituted phenyl ring. The observation of the new signals from ABDC and their increasing intensity within the series as well as the slight shift of signals upon substitution clearly demonstrate the incorporation of both linkers in the structure.

The thermal stability of the MIXMOFs was investigated using TG and DTG. Since the thermal stability of pure MIL-53 (ca. 500 °C) is higher than that of NH₂-MIL-53 (ca. 410 °C), decomposition of the MIXMOFs should be dependent on the BDC/ABDC ratio. From the DTG curves (Fig. 4, top) it can be seen that the maximum of the decomposition rate is shifted from 593 °C for the MIXMOF with 10% of ABDC to 537 °C (50% ABDC) and 494 °C (90% ABDC), respectively. Thermal decomposition of the three materials starts at temperatures between 460 °C (10% ABDC) and 410 °C (90% ABDC; see TG, Fig. 4, bottom).

In summary, we have proven that the MIXMOF concept could successfully be transferred to MIL-53(Al). The synthesis of isorecticular mixed-linker MOFs bearing both BDC and ABDC linkers using solvothermal synthesis was proven by powder X-ray diffraction. The increasing amount of functionalized ABDC linkers could be visualized using both IR and solid-state NMR spectroscopy. Thermal analysis revealed that the thermal stability of the MIXMOFs is dependent on the ratio of the two linker molecules and can be tuned within the limits set by the pure materials MIL-53(Al) and NH₂-MIL-53(Al).

As a consequence, the MIXMOF concept facilitates the synthesis of materials with tunable number of functional sites which allows for the rational design of new materials with optimized properties for post-synthetic modification and/or catalytic applications (thermal stability, number and distribution of active sites) which are currently under investigation.

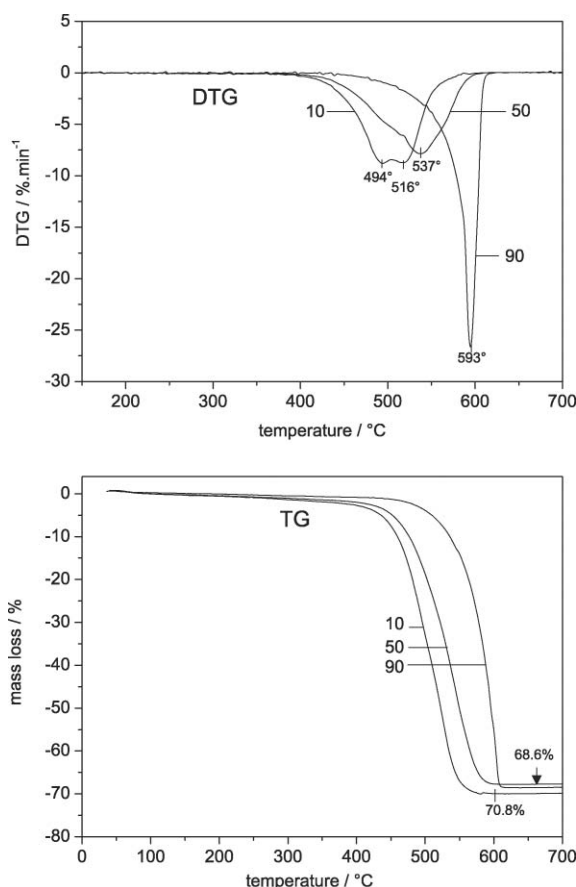


Fig. 4 TG (top) and DTG (bottom) curves of the MIXMOFs (10-90% of ABDC; 20% O₂, balance He, heating rate: 10 K min⁻¹).

Notes and references

- S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334–2375.
- A. K. Cheetham, C. N. R. Rao and R. K. Feller, *Chem. Commun.*, 2006, 4780–4795.
- G. Férey, *Chem. Soc. Rev.*, 2008, **37**, 191–214.
- O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705–714.
- U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt and J. Pastré, *J. Mater. Chem.*, 2006, **16**, 626–636.
- M. Sabo, A. Henschel, H. Fröde, E. Klemm and S. Kaskel, *J. Mater. Chem.*, 2007, **17**, 3827–3832.
- S. Opelt, S. Türk, E. Dietzsch, A. Henschel, S. Kaskel and E. Klemm, *Catal. Commun.*, 2008, **9**, 1286–1290.
- F. Schröder, S. Henke, X. Zhang and R. A. Fischer, *Eur. J. Inorg. Chem.*, 2009, 3131–3140.
- L. Alaerts, E. Séguin, H. Poelman, F. Thibault-Starzyk, P. A. Jacobs and D. E. De Vos, *Chem.–Eur. J.*, 2006, **12**, 7353–7363.
- F. X. Llabres i. Xamena, A. Abad, A. Corma and H. Garcia, *J. Catal.*, 2007, **250**, 294–298.
- J. Gascon, U. Aktay, M. D. Hernandez-Alonso, G. P. M. van Klink and F. Kapteijn, *J. Catal.*, 2009, **261**, 75–87.
- T. Ahnfeldt, D. Gunzelmann, T. Loiseau, D. Hirsemann, J. Senker, G. Férey and N. Stock, *Inorg. Chem.*, 2009, **48**, 3057–3064.
- Z. Wang and S. M. Cohen, *Angew. Chem., Int. Ed.*, 2008, **47**, 4699–4702.
- Z. Wang and S. M. Cohen, *J. Am. Chem. Soc.*, 2009, **131**, 16675–16677.
- S.-H. Cho, B. Ma, S. T. Nguyen, J. T. Hupp and T. E. Albrecht-Schmitt, *Chem. Commun.*, 2006, 2563–2565.
- K. C. Szeto, C. Prestipino, C. Lamberti, A. Zecchina, S. Bordiga, M. Bjørn, M. Tilset and K. P. Lillerud, *Chem. Mater.*, 2007, **19**, 211–220.
- A. D. Burrows, C. G. Frost, M. F. Mahon and C. Richardson, *Angew. Chem., Int. Ed.*, 2008, **47**, 8482–8486.

- 18 K. Koh, A. G. Wong-Foy and A. J. Matzger, *Chem. Commun.*, 2009, 6162–6164.
- 19 W. Kleist, F. Jutz, M. Maciejewski and A. Baiker, *Eur. J. Inorg. Chem.*, 2009, 3552–3561.
- 20 W. Kleist, M. Maciejewski and A. Baiker, *Thermochim. Acta*, 2010, **499**, 71–78.
- 21 K. M. L. Taylor-Pashow, J. Della Rocca, Z. Xie, S. Tran and W. Lin, *J. Am. Chem. Soc.*, 2009, **131**, 14261–14263.
- 22 T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille and G. Férey, *Chem.–Eur. J.*, 2004, **10**, 1373–1382.
- 23 T. K. Trung, P. Trens, N. Tanchoux, S. Bourrelly, P. L. Llewellyn, S. Loera-Serna, C. Serre, T. Loiseau, F. Fajula and G. Férey, *J. Am. Chem. Soc.*, 2008, **130**, 16926–16932.
- 24 L. Alaerts, M. Maes, L. Giebeler, P. A. Jacobs, J. A. Martens, J. F. M. Denayer, C. E. Kirschhock and D. E. De Vos, *J. Am. Chem. Soc.*, 2008, **130**, 14170–14178.