THE ARRANGEMENT OF LINKERS IN MOFS:
A SOLID-STATE NMR VIEW

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ABSTRACT

Herein we present a simple NMR-based approach to inspect the distribution of two (or more) different linkers over the mixed-linker metal-organic frameworks. We show the limitations of this technique and highlight the advantages over complementary NMR methods. The performance of the approach is demonstrated with an example of Al-based metal-organic framework DUT-5, which has two different linkers incorporated into its framework.

Keywords: linker distribution, metal-organic frameworks, modeling, NMR spectroscopy, proton spin diffusion.

INTRODUCTION

Metal-organic frameworks (MOFs) are advantageous over other porous materials because of the versatility of their frameworks and the simplicity of the synthesis. For example, if the organic or metallic precursors are changed, a new material with different macroscopic properties can be prepared. Furthermore, one can have an effect on framework geometry and size of the pores by adjusting the synthesis conditions. Therefore, MOFs can be used in a variety of applications, ranging from gas adsorption/separation to chemical sensing, catalysis, etc.[1,2]

A step further is mixing different linkers through which new MOFs with combined properties of each of the incorporated linkers can be synthesized. Usually these materials are isostructural to the single-linker frameworks and there are not many techniques that can be used for their precise characterization. Deng et al.[3] confirmed the successful incorporation of different linkers by dissecting large single crystals of MOF-5 into three equal segments. Each segment of the crystal was subjected to acid digestion after which the fraction of different linkers was determined by the solution ^{1}H NMR. Kong et al.[4] were able to tell even something about the arrangement of the linkers in MOF-5. They enriched various linkers in the synthesis with ^{15}N and carried out demanding ^{13}C-^{15}N REDOR NMR measurements, which gave important information about "average distance" between crystallographically inequivalent carbon and nitrogen nuclei. By comparing the experimental data to the calculated ones, they were able to distinguish four different linker apportionments (large clusters, small clusters, random distribution, and alternating distribution). In this work we proposed a new approach to resolving linkers arrangement in mixed-linker metal-organic frameworks (ML-MOFs) and demonstrated its performance on Al-based mixed-linker DUT-5 (ML-DUT-5), whose framework consists of biphenyl dicarboxylic (BPDC) and bipyridyl dicarboxylic (BPyDC) linkers.

EXPERIMENTAL

Synthesis of ML-DUT-5 was based on the procedure described by Senkovska et al. for single-linker DUT-5[5], except that 15% of the 4,4'-biphenyldicarboxylic acid was replaced by 2,2′-bipyridine-5,5′-dicarboxylic acid in the synthesis mixture.

[1]H MAS, [1]H-^{13}C CPMAS and ^{1}H Spin diffusion NMR spectra of ML-DUT-5 have been recorded on the 600 MHz Varian NMR system equipped with the Varian 3.2 mm probe.

First-principles calculations were carried out using the density functional theory in the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA PBE)[6] with plane wave basis and ultrasoft pseudopotentials, as implemented in the CASTEP code.

RESULTS AND DISCUSSION

The proposed approach is based on non-demanding and fast two-dimensional ^{1}H spin-diffusion NMR experiment, which probes the proximities between inequivalent protons. When the two protons are close to each other, a cross-peak appears at their frequency cross section. The intensity of the cross peak represents the amount of the polarization that was transferred during the mixing period. By acquiring a series of two-dimensional experiments, each at different mixing time, we can obtain build-up curves for the polarization transfer between inequivalent protons. Those build-up curves can also be calculated using semi-empirical equations, if we know the precise structure.[7] To determine the arrangement of different linkers in ML-MOFs, one has to build several models with different linker apportionments, calculate all build-up curves for each of them, and make a comparison to the experimental data. The model that best describes the measured curves is the right one.

The only requirement for this approach to be applicable is that at least one ^{1}H NMR signal of one linker has to be resolved from at least one ^{1}H NMR signal of another linker. Thus the correct assignment of ^{1}H NMR signals is crucial. In case of ML-DUT-5, the ^{1}H MAS assignment was supported by the [1]H-^{13}C LG-HETCOR experiment and DFT/GIPAW calculation.[8] We managed to resolve the H1 atoms of BPDC and the H2' atoms of BPyDC from the other signals (Figure 1).
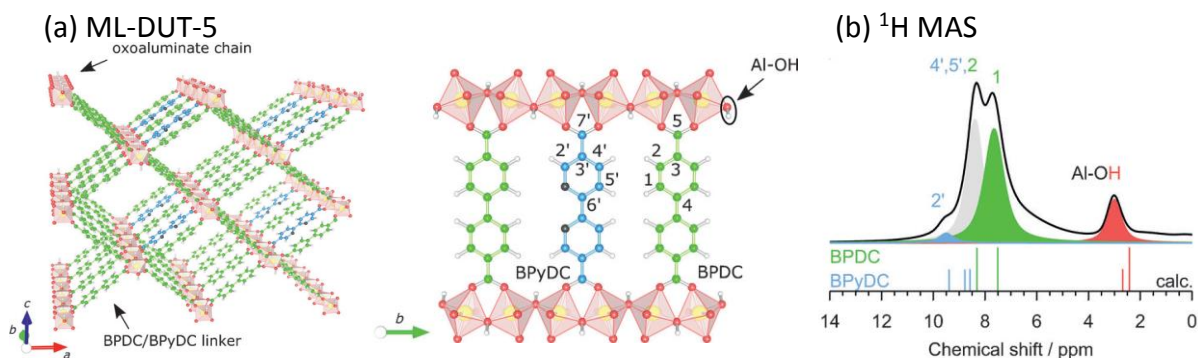

Figure 1. (a) Structure and labeling of hydrogen atoms of ML-DUT-5. Biphenyl and bipyridyl dicarboxylic linkers are colored green and blue, respectively. (b) ^{1}H MAS spectrum of ML-DUT-5. Vertical lines mark the calculated ^{1}H isotropic chemical shifts.
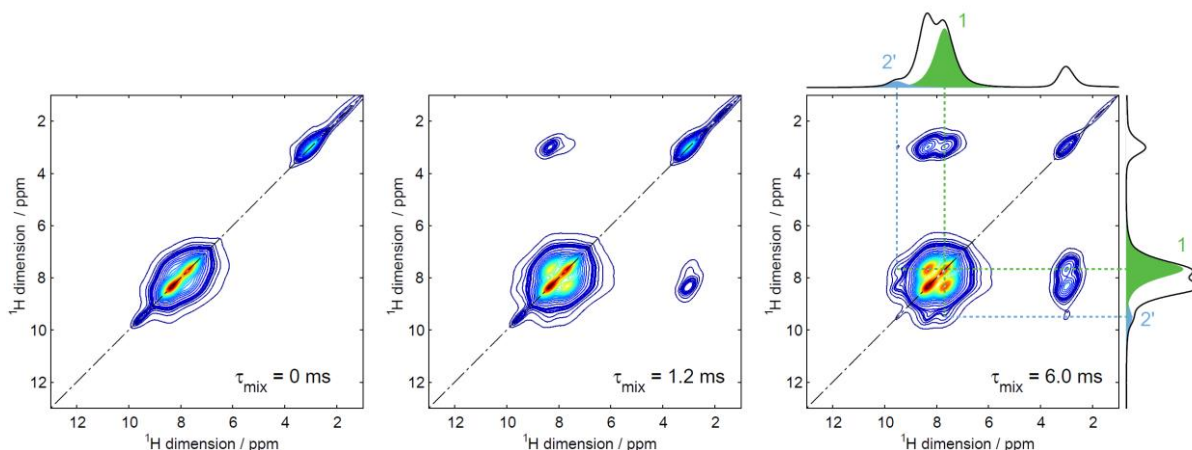
Figure 2. ^{1}H spin-diffusion spectra of ML-DUT-5 for three different mixing periods. Horizontal and vertical dotted lines mark the frequencies of the H2' and H1 resonances, and their crossings mark the H2'–H1 cross-peaks.

After the successful assignment of ^{1}H MAS spectrum, a series of 29 two-dimensional ^{1}H spin-diffusion spectra were measured with mixing times ranging between 0 and 6.4 ms (Figure 2). The build-up curves were collected from ^{1}H spin-diffusion spectra by fitting all cross-peaks with a sum of two-dimensional Pseudo-Voigt functions. We built several models with different distributions of both linkers over the framework, and calculated build-up curves. The best agreement between the calculated and measured curves was for the model in which the minority BPyDC linker was homogeneously distributed throughout the framework (Figure 3a).
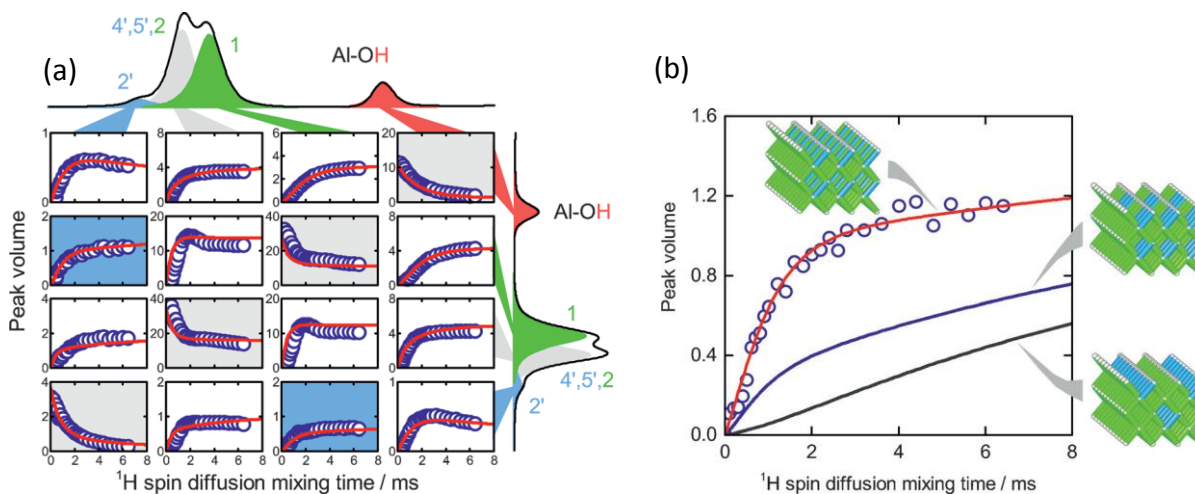

Figure 3. (a) Measured and calculated ^{1}H spin-diffusion curves for ML-DUT-5. The calculated curves were obtained with the model in which BPyDC linkers were homogeneously distributed within the framework. (b) Measured and calculated ^{1}H spin-diffusion curves of the cross-peak H2'-H1. Results of calculations for three different models of ML-DUT-5 are presented. Only the model with a homogeneously distributed BPyDC linker leads to good agreement with the experimental data.

The cross-peak evolution between H1 and H2' proton was essential for the final determination of the linkers arrangement in ML-DUT-5. As soon as a BPyDC linker does not have BPDC linkers as nearest neighbors within the layer along the crystallographic *b* axis (along which the distances between the neighboring linkers are the shortest), the predicted polarization transfer between H2' and H1 becomes much slower than the measured value (Figure 3b). Such information about the distribution of BPyDC and BPDC linkers within ML-DUT-5 cannot be

obtained by any other approach except the more demanding and much more expensive approach based on the ^{13}C–^{15}N REDOR NMR experiment and ^{15}N isotopically enriched material.

CONCLUSION

We have shown that a simple ^1H spin-diffusion NMR experiment enables an insight into the distribution of linkers in mixed-linker MOFs. The assignment of ^1H MAS spectrum plays a crucial role and can be more experimentally and computationally demanding that the measurement and modeling of spin-diffusion curves. If all the requirements are met, this approach is more convenient and less expensive than previously mentioned techniques.[3,4] We demonstrated its performance for the case of ML-DUT-5, where we concluded that the minority linker is well dispersed throughout the framework and does not form single-linker domains.

REFERENCES

[1] S. T. Meek, J. a. Greathouse and M. D. Allendorf, *Adv. Mater.*, 2011, **23**, 249–267.

[2] A. U. Czaja, N. Trukhan and U. Müller, *Chem. Soc. Rev.*, 2009, **38**, 1284–1293.

[3] H. Deng, C. J. Doonan, H. Furukawa, R. B. Ferreira, J. Towne, C. B. Knobler, B. Wang and O. M. Yaghi, *Science*, 2010, **327**, 846–850.

[4] X. Kong, H. Deng, F. Yan, J. Kim, J. A. Swisher, B. Smit, O. M. Yaghi and J. A. Reimer, *Science*, 2013, **341**, 882–885.

[5] I. Senkovska, F. Hoffmann, M. Fröba, J. Getzschmann, W. Böhlmann and S. Kaskel, *Microporous Mesoporous Mater.*, 2009, **122**, 93–98.

[6] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865–3868.

[7] B. Elena, L. Emsley, *J. Am. Chem. Soc.*, 2005, **127**, 9140–6.

[8] A. Krajnc, T. Kos, N. Zabukovec Logar and G. Mali, *Angew. Chemie Int. Ed.*, 2015, **54**, 10535–10538.