

WHAT CAN NMR TELL US ABOUT STRUCTURAL IMPERFECTIONS IN MOFs?

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ABSTRACT

Metal-organic framework materials (MOFs) have been studied for more than two decades, but only recently, with the discovery of inherent defects in their frameworks, the center of interest was diverted to the structural imperfections. Such imperfections should be carefully examined since they can greatly alter macroscopic properties of the bulk MOFs (e.g., catalytic activity, adsorption affinity, optical properties). Herein we report the observation of the local distortions after framework amorphization of ZIF-76. Using advanced solid-state NMR techniques we show that both linkers forming the crystalline counterpart are still well mixed after melt-quenching and that only slight contractions of the linkers occur.

Keywords: metal-organic frameworks, melt-quenched glass, solid-state NMR, proton spin diffusion.

INTRODUCTION

MOFs are the largest subgroup of nanoporous materials. More than 20,000 structures have been reported and studied after their first introduction in the 1990s. The majority of studies were focused on their crystalline nature, but the discovery that some of them inevitably contain defects and that sometimes material properties could not be fully explained, ignited this relatively young and fast-growing research field of defects and disorder in MOFs [1–3]. Nowadays, it is known that many important properties such as mechanical stability, catalytic activity, the kinetics of guest molecules, and optical properties often emerge from the presence of non-periodic parts of the framework. The question of their extent and spatial arrangement in the material needs to be addressed carefully.

In order to achieve the desired properties of the material, defects can be introduced deliberately. In our previous work, we proposed the mixed-linker approach for defect engineering [4]. UiO-66 material was prepared by mixing together two structurally distinct but dimensionally equivalent linkers with different thermal stability. After heating the crystalline powder to 325 °C the labile linker was decomposed and removed from the framework leaving missing-linker defects behind. An NMR experiment which probes the rate of polarization transfer between magnetically inequivalent protons [5] played a key role in the discovery that the labile linker was homogeneously dispersed along the framework prior to the thermal treatment. This explained the highest density of coordinatively unsaturated metal sites in UiO-66 after the treatment and coincided well with the results of other experimental methods. The same approach was later used to study disorder after post-synthetic linker exchange in UiO-66 and defects distribution in Ti-based COK-47 [6,7].

A special example of mixed-linker MOFs are zeolitic imidazolate frameworks (ZIFs). Some of their representatives have the ability to be amorphized (prepared as glasses) by melting (and quench cooling) of crystalline counterparts. Moreover, they tend to be very good glass formers [8]. Even though many crystalline ZIFs are porous, the glasses prepared through vitrification of these ZIFs were thus far dense. The first successful preparation of a microporous glass started from the crystalline ZIF-76 with imidazolate (Im) and chloro- (ClbIm) or methyl-benzimidazolate (mbIm) ligands, and with large-pore LTA topology [9].

The presented study is focused on the short-range structural changes of the vitreous state of ZIF-76-mbIm that occur during melt-quenching.

EXPERIMENTAL

For the synthesis of ZIF-76-mbIm ($\text{Zn}(\text{Im})_{1.33}(\text{5-mbIm})_{0.67}$), the procedures described by Peralta et al. [10] were followed, except that 5-methylbenzimidazole was used in place of 5-chloroimidazole. For the vitrification, a bulk powder sample was placed into a ceramic crucible and then into a tube furnace, where it was heated to 471 °C under argon with a heating rate of 10 °C min⁻¹. Upon reaching the set temperature, the furnace was turned off and the sample cooled naturally (under argon) to room temperature.

Solid-state NMR experiments were carried out on a 600 MHz Varian NMR system equipped with a 1.6 mm Varian HXY MAS probe. Larmor frequencies for ¹H and ¹³C were 599.50 MHz and 150.74 MHz, respectively, and sample rotation frequency was 40 kHz. For 1D ¹H and ¹³C MAS measurements, ¹H and ¹³C 90° excitation pulses of 1.65 μs and 1.5 μs were used, respectively. In ¹H MAS NMR measurements 8 scans were co-added and repetition delay between scans was 3 s. In ¹³C MAS NMR measurements number of scans was 5500 and repetition delay was 30 s. Frequency axes of ¹H and ¹³C spectra were referenced to tetramethylsilane. For each of 12 increments along the indirectly-detected dimension of two-dimensional ¹³C-detected proton spin-diffusion measurement, 4000 scans were acquired and the repetition delay between each two consecutive scans was 0.5 s. During mixing periods, the radio frequency driven dipolar recoupling (RFDR) scheme was used to enhance homonuclear dipolar coupling among protons. The ¹H-¹³C cross-polarization (CP) transfer step utilized Lee-Goldburg CP conditions.

RESULTS AND DISCUSSION

The chemical environments, distribution and geometrical changes of the framework linkers were studied in both crystalline and melt-quenched forms of ZIF-76-mbIm. Solid-state ¹H and ¹³C magic-angle spinning (MAS) NMR spectroscopic measurements were carried out for this purpose. ¹H MAS NMR measurements on an evacuated crystalline sample yielded a broad signal at 6–7 ppm arising from both Im and mbIm protons and an additional peak at 1.5–2 ppm, belonging to the methyl functional group of the benzimidazolate ring (Figure 1a). The ¹³C MAS NMR spectrum exhibited several resolved signals, matching those expected from the chemical structures of the linkers (Figure 1b). The intensity ratio between the corresponding signals matched well the chemical composition of the material. Vitrification led to a notable broadening of the spectra related to the increased disorder, but the chemical shifts remained rather unchanged, aside from the small ¹³C shift of the methyl group to lower field. These results demonstrate that the chemical environments of the linkers in the glass are broadly similar to those in their crystalline precursors.

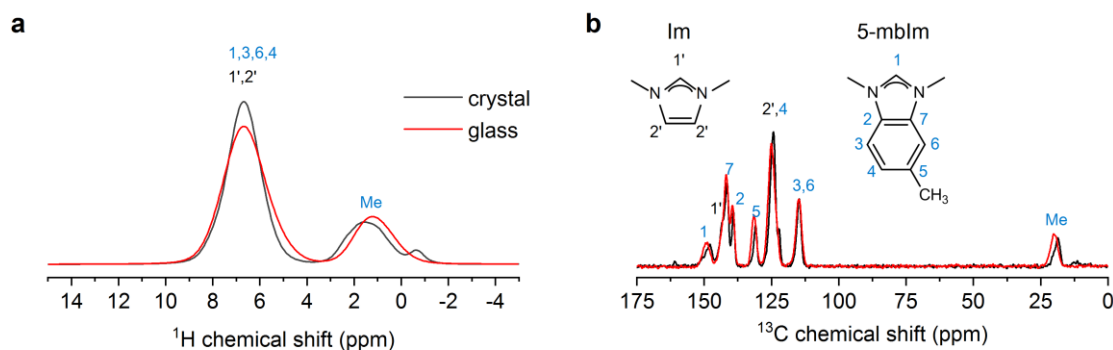


Figure 1. (a) ¹H MAS and (b) ¹³C MAS NMR spectra of crystalline (black) and amorphous/glass (red) forms of ZIF-76-mbIm. The peaks were assigned based on 2D hetero-nuclear correlation NMR experiments.

The distributions of the linkers within both crystal and glass phases were investigated using proton spin-diffusion (PSD) NMR spectroscopy. The rate of polarization transfer between protons strongly depends on their proximities and from the two-dimensional experiments, one can extract the average distances between chemically inequivalent protons. To resolve distinct ¹H contributions in the aromatic region (6-7 ppm), the polarization was transferred from protons to carbon nuclei before the acquisition of the signal [11]. A series of 2D PSD measurements with different mixing times were performed to track the transfer of proton polarization from the methyl group protons (2 ppm) to all other protons in the sample (6-7 ppm). Off-diagonal peaks were then analyzed and the build-up curves obtained (Figure 2). The slope of such build-up curve represents the polarization transfer rate within the selected pair of protons, and the rate is in tight relation with the average distance between the selected protons. The time at which the plateau is reached indicates the degree of homogeneity. We focused on the polarization transfer from the methyl group to H1 protons of the 5-methylbenzimidazole (intra-linker transfer) and to H1' protons of the imidazole (inter-linker transfer). In both crystalline and glass ZIF-76-mbIm, the inter-linker transfer of polarization was observed to be faster than intra-linker transfer, implying that the linkers are well mixed within the framework before and after melt-quenching and do not separate into domains. However, an even steeper initial part for the glassy sample suggests that the distances between 5-methylbenzimidazole and imidazole linkers contract slightly upon vitrification. This is consistent with the ¹³C downfield shift of the methyl group resonance, which may arise from the close contacts with the π electron clouds of neighbouring linkers. Furthermore, the intra-linker polarization transfer is faster in glass, which can be explained with slight deformations/bending of the bulky linkers during vitrification.

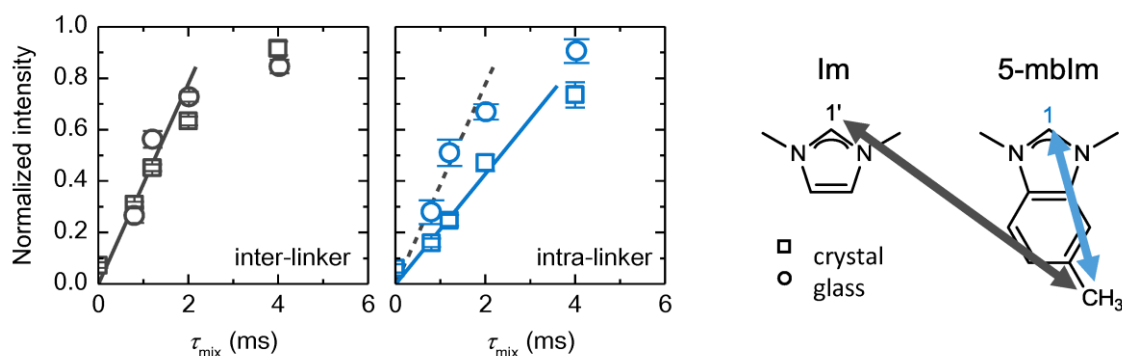


Figure 2. Proton spin-diffusion build-up curves of crystalline and glass phases of ZIF-76-mbIm (left) and the schematic representation of the inter-linker and intra-linker proton pairs that give rise to these curves (right).

CONCLUSION

Solid-state NMR has proven as a very powerful technique for studying disordered MOFs in general, but the advanced experiments can be applied to various heterogeneous solids. In the case study, ZIF-76-mbIm undergoes only slight structural deformations upon vitrification. The arrangement of the linkers and the ratio between them are both preserved, which crucially contributes to the fact that the melt-quenched ZIF-76-mbIm is the first glass with a permanent accessible porosity, obtained without any post-synthetic treatment.

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