A Simple NMR-based Tool for Studying the Spatial Distribution of Linkers within Mixed-Linker Metal-Organic Frameworks

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One of key advantages of metal-organic framework materials (MOFs) over other porous materials is the versatility of their frameworks, which can be prepared from many different organic linkers and can be functionalized with many different functional groups. Even a single-phase MOF can contain various linkers or functional groups. For example, Deng et al. prepared a series of MOFs by mixing differently modified terephthalic acids bearing -H, -NH₂, -Br, -Cl, -NO₂, -(CH₃)₂, -C₄H₄, -(OC₃H₅)₂, and -(OC₂H₅)₂ groups in different relative amounts and combinations. It was shown that selectivity of such mixed-linker MOFs crucially depended on the way the different linkers or functional groups were distributed throughout the crystals. Until recently, only two attempts of the determination of the distribution of different linkers within mixed-linker MOFs have been presented. Deng et al. divided large single crystals of mixed-linker MOF-5 into three equal segments and determined the fractions of different linkers in the segments. Kong et al. isotopically labeled various linkers used in the synthesis of MOF-5 with ¹⁵N and carried out demanding ¹³C-¹⁵N REDOR NMR measurements, which provided information on the average distances among different linker molecules. By comparing the results of the REDOR measurements with results from Monte Carlo simulations, they were able to discriminate between cases where linkers of one type formed homogeneous domains within crystals, where different linkers were alternating with one another in the framework, and where different linkers were distributed randomly throughout the crystalline framework.

Recently, we have shown that a relatively simple NMR method that does not require isotopic labeling can also provide valuable insight into the distribution of linkers in mixed-linker MOFs. The proposed approach is based on variable-contact-time ¹H spin-diffusion NMR measurements and modeling of spin-diffusion curves with semi-empirical equations. Because ¹H nuclei are observed, there are no difficulties with the sensitivity of the experiment, but there can be problems with the resolution. For the approach to be applicable, one has to be able to resolve at least one ¹H NMR signal of one linker from at least one ¹H NMR signal of another linker. Correct assignment of ¹H NMR signals is also crucial. In our test case, assignment was supported by the ¹H,¹³C LG-HETCOR experiment and DFT/GIPAW calculation. In fact, the assignment of NMR signals can be more experimentally and computationally demanding than the measurement and modeling of spin-diffusion curves; however, it has to be carried out only once for a given mixed-linker system. Samples obtained in different syntheses or with different ratios of the two linkers can then be inspected quickly using only ¹H spin-diffusion experiments. The described approach could be very useful for the inspection of various mixed-linker MOFs.