Paramagnetic Ion Doping in MOFs to Accelerate Solid-State NMR Measurements

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Metal-organic frameworks (MOFs) are porous materials formed by metal ions and organic ligands that have been studied for gas adsorption and other applications. Solid-state NMR (SSNMR) is a powerful method in the study of local static and dynamic structures of MOFs. However, in many cases, weakness and slow relaxation rate of the NMR signal require multiple scans and a long waiting time for each scan, respectively, which lengthens the measurement time. Therefore, it is important to develop a method to shorten the measurement time to facilitate MOF research using SSNMR.

Cross-polarization (CP) can transfer the magnetization of abundant ^{1}H spins to dilute nuclear spins (^{13}C, ^{15}N, etc.) and is frequently used to enhance the intensity of the SSNMR signal. Paramagnetic metal ion doping into the sample can accelerate the NMR measurement because the interaction of the nuclear spins with the electron spins of the paramagnetic ions promotes nuclear spin relaxation.[1] In this study, we aim to accelerate CP NMR measurements of MOFs by doping paramagnetic metal ions in MOFs using a metal solid-solution approach.

ZIF-8 $[Zn(2\text{-}MeIm)_2]_n$ was synthesized with various Co^{2+} doping ratios,[2] and ^{13}C CP and ^{1}H relaxation time measurements were performed. To find the optimal doping ratio, we formulated the signal acquisition efficiency per unit time (= signal-to-noise ratio/measurement time) relative to the doping ratio of paramagnetic ions and investigated the relationship between the doping ratio and the efficiency using the experimental signal intensity, linewidth, and relaxation time. Fig. 1 shows the obtained acquisition efficiency normalized to the efficiency of the undoped sample. The highest acquisition efficiency is 3.7 at a doping ratio of 0.3%. Excessive doping can reduce CP efficiency and broaden the signal due to overly fast relaxation, which in turn reduces the measurement sensitivity and the acquisition efficiency.

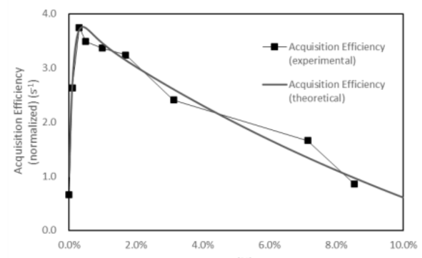

Fig. 1: Normalized acquisition efficiency relative to doping ratio

To demonstrate the effectiveness of this method, we performed ligand dynamics analysis on Co^{2+}-doped MOF-5 $[Zn_4O(1,4\text{-benzodicarboxylate})_3]_n$ using 2D ^{13}C SSNMR. The results will be discussed on the day of the presentation.

1) N. P. Wickramasinghe, et al., *Nat. Methods* **2009**, *6*, 215. 2) G. Kaur, et al., *J. Mater. Chem. A* **2016**, *4*, 14932.