NRC Publications Archive Archives des publications du CNRC

Characterization of Zn-containing metal–organic frameworks by solid-state ^{67}Zn NMR spectroscopy and computational modeling

Sutrisno, Andre; Terskikh, Victor V.; Shi, Qi; Song, Zhengwei; Dong, Jinxiang; Ding, San Yuan; Wang, Wei; Provost, Bianca R.; Daff, Thomas D.; Woo, Tom K.; Huang, Yining

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<https://doi.org/10.1002/chem.201201563>

Chemistry : a European Journal, 18, 39, pp. 12251-12259, 2012-09-03

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=9fcc2fd1-9ea4-4af8-8efa-dbe4026270af>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=9fcc2fd1-9ea4-4af8-8efa-dbe4026270af>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

Characterization of Zn-containing MOFs by Solid-state ^{67}Zn NMR and Computational Modeling

Dr. Andre Sutrisno,^a Dr. Victor V. Tersikh,^b Qi Shi,^c Zhengwei Song,^c Prof. Jinxiang Dong,^{c,} San Yuan Ding,^d Prof. Wei Wang,^{d,*} Bianca R. Provost,^e Dr. Thomas D. Daff,^e Prof. Tom K. Woo^{e,*} and Prof. Yining Huang^{a,*}*

^aDepartment of Chemistry, The University of Western Ontario, London, Ontario, Canada, N6A 5B7. Email: yhuang@uwo.ca, Tel: 519-661-2111 x86384. ^bMeasurement Science and Standards, National Research Council, Ottawa, Ontario, Canada K1A 0R6. ^cResearch Institute of Special Chemicals, Taiyuan University of Technology, Shanxi, Taiyuan 030024, P.R. China. Email: dongjinxiaingwork@hotmail.com. ^dState Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu, 730000, P. R. China. Email: wang_wei@lzu.edu.cn. ^eCentre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada, K1N 6N5. Email:

Tom.Woo@uottawa.ca

RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

ABSTRACT. Metal-organic frameworks (MOFs) are an extremely important class of porous materials with many applications. The metal centers in many important MOFs are zinc cations. However, their Zn environments have not been characterized directly by ^{67}Zn solid-state NMR (SSNMR). This is because ^{67}Zn ($I = 5/2$) is unreceptive with many unfavorable NMR characteristics, leading to very low sensitivity. In this work, we report, for the first time, a ^{67}Zn natural abundance SSNMR spectroscopic study of several representative ZIFs (zeolitic imidazolate frameworks) and MOFs at ultrahigh magnetic field of 21.1 T. Our work demonstrates that ^{67}Zn MAS (magic-angle spinning) NMR spectra are highly sensitive to local Zn environment and can differentiate non-equivalent Zn sites. The ^{67}Zn NMR parameters can be predicted by theoretical calculations. Through the study of MOF-5 desolvation, we show that with the aid of computational modeling, ^{67}Zn NMR can provide valuable structural information on the MOF systems whose structures are not well described. Using ZIF-8 as an example, we further demonstrate that ^{67}Zn NMR is highly sensitive to the guest molecules present inside the cavities. Our work also shows that a combination of ^{67}Zn NMR data and molecular dynamics simulation can reveal detailed information on the distribution and the dynamics of the guest species. The present work establishes ^{67}Zn SSNMR spectroscopy as a new tool complementary to X-ray diffraction for solving outstanding structural problems and for determining the structures of many new MOFs yet to come.

Introduction

One of the most exciting advances in the field of nanoporous materials in recent years is the emergence of a fascinating family of hybrid organic-inorganic solids, known as metal-organic frameworks (MOFs).^[1, 2] They have many potential industrial and technological applications in areas of catalysis, ion-exchange, sensors and, in particular, gas storage and separation. Characterization is important because understanding the relationship between the key properties of these materials and their unique structures is crucial to the development of new applications and the performance improvement of their current uses.

Although the structures of many MOFs can be determined by single crystal X-ray diffraction, a significant number of MOF structures have to be refined from more limited powder XRD data due to the lack of suitable single crystals.^[3] In such cases an unambiguous structure solution requires additional information from complementary techniques. Solid-state NMR (SSNMR) spectroscopy is a complementary technique to X-ray diffraction for structural characterization, which provides invaluable information on local environment around the nucleus of interest.^[4, 5] Indeed, ^1H and ^{13}C SSNMR spectroscopy has been routinely used for framework characterization. Using the deuterated organic linker, ^2H NMR is used to examine the flexibility of the framework.^[6-8] The dynamics of the guest species can also be probed by ^2H NMR.^[6, 9] ^{129}Xe NMR has been utilized to study the porosity.^[10-12] Characterization of MOFs by ^{11}B and ^{17}O SSNMR has also been reported.^[13, 14] Very recently, the utility of DNP (dynamic nuclear polarization) - enhanced ^{13}C and ^{15}N SSNMR in MOF characterization has been demonstrated.^[15] To properly characterize MOF structure, the local environment around

metal center needs to be carefully examined. To this end, SSNMR studies of several highly receptive nuclei such as ^{27}Al , ^{45}Sc and ^{71}Ga has been employed to directly characterize the metal local structure and proven to be a very sensitive probe.^[16-18]

For many important MOFs, their metal centers are zinc cations. The best known examples include the IRMOF (isoreticular MOF)^[19, 20] and ZIF (zeolitic imidazolate framework)^[21, 22] series. In principle, ^{67}Zn SSNMR spectroscopy should be an ideal tool for directly probing the Zn environment in MOFs. However, the local structure around zinc center in MOFs has never been directly characterized by SSNMR spectroscopy. This is primarily because ^{67}Zn ($I = 5/2$), the only NMR active isotope of zinc, has several unfavourable NMR characteristics. It has a low gyromagnetic ratio (γ), low natural abundance (4.1 %), and a relatively large nuclear quadrupole moment, resulting in low-sensitivity and broad resonances. Despite these problems, NMR studies on metallic zinc,^[23] simple inorganic zinc salts,^[24-30] organozinc complexes,^[31-35] zinc-containing macromolecules^[36] and proteins^[37] have been documented in the literature. For the most recent survey of ^{67}Zn SSNMR studies, the readers are referred to the paper by Power *et.al.*^[38] It should be pointed out that in addition to the unfavourable NMR properties mentioned earlier, a problem specific to the MOF systems is the extremely low zinc concentrations due to their low densities. For the MOFs examined in this work, the number of ^{67}Zn atoms per nm^3 ranges from 0.10 to 0.15 (Table S1). For comparison, this number for bulk ZnO (with wurtzite structure) is $1.7 \text{ }^{67}\text{Zn atoms} / \text{nm}^3$.^[39]

In the present work, we report the first natural abundance ^{67}Zn SSNMR study of Zn environment in several representative MOFs using an ultrahigh field of 21.1 T. Several important ZIFs with known structures (ZIF-8, ZIF-14, ZIF-4, ZIF-7)^[21, 40-42] are

first examined to demonstrate that the ^{67}Zn NMR spectra are sensitive to the Zn local structure. The results are then used as a benchmark to investigate the MOFs whose structures are not well characterized. In this regard, we obtained structural information on several MOF-5 samples with different degrees of solvation. Furthermore, using ZIF-8 as an example, we show that the ^{67}Zn NMR spectra are also sensitive to the guest species present in the pores and therefore can provide valuable information on host-guest interactions. The work demonstrates that combination of ^{67}Zn SSNMR spectroscopy and computational modeling and simulation is an effective approach to characterize local Zn environments in MOFs.

Results and Discussion

We first examined ZIF-8 and ZIF-14. One of the reasons for choosing these two materials is because they each only have a single Zn site in their crystal structures, which simplifies the analysis of the spectra. ZIF-8 ($\text{Zn}[\text{MIm}]_2$, MIm = 2-methylimidazolate) is a prototypical and the most well-known ZIF compound with a SOD zeotype structure.^[21, 41] Indeed, the ^{67}Zn MAS NMR spectrum (Figure 1a) of as-synthesized ZIF-8 displays a single narrow peak, which does not exhibit a typical quadrupolar line-shape. The symmetric line-shape and very small FWHH (full width at half height) that is less than 1 kHz indicate a small quadrupolar interaction experienced by the Zn. The resonance of the MAS spectrum at 21.1 T is too narrow to extract the C_Q accurately. To better determine the C_Q , we acquired the static spectra at 9.4 T and 21.1 T. Figure S1 shows that the total width of the powder pattern approximately scales inversely with the magnetic field (*ca.* 3 kHz for 9.4 T and 1.5 kHz for 21.1 T), indicating that the pattern is not from a

distribution of chemical shift or quadrupolar interaction and that although the C_Q is small (1.1 MHz), the spectrum is dominated by the second-order quadrupolar interaction. The small C_Q implies that the Zn has a relatively high spherically symmetrical environment resulting in a small electric field gradient (EFG) at the Zn site. The result is indeed consistent with the reported crystal structure,^[21] which shows that the ZnN_4 tetrahedron is almost perfect, *i.e.*, Zn–N bonds are all equal (1.987 Å) and N–Zn–N angles are almost perfect tetrahedral angles ($109.3^\circ \times 4$; $109.8^\circ \times 2$).

Figure 1b shows the ^{67}Zn MAS spectrum of as-made ZIF-14 ($\text{Zn}[\text{Elm}]_2$, Elm = 2-ethylimidazolate).^[41, 42] The spectrum is also narrow (the line width is only about 2.8 kHz), but it is broader than that of ZIF-8 and has a distinct line-shape due to the second-order quadrupolar interactions. The spectrum can be well fitted with a single Zn site and the simulations generated a set of ^{67}Zn EFG tensor parameters: $C_Q = 2.8(1)$ MHz, $\eta_Q = 0.85(5)$ and $\delta_{\text{iso}} = 260(5)$ ppm. Observing one Zn signal is consistent with the reported ZIF-14 crystal structure.^[41] The $C_Q(^{67}\text{Zn})$ value in ZIF-14 is larger than that in ZIF-8, which is due to a slightly more distorted ZnN_4 tetrahedral unit, as reflected by the larger distributions of the Zn–N bond distances (2.001–2.017 Å) and N–Zn–N bond angles (104.4 – 112.6°). The distinct line-shape corresponding to a non-zero η_Q indicates that the EFG tensor at the Zn nucleus is not axially symmetric, which is in agreement with the low (2-fold) site symmetry.

Since many ZIF materials have more than one Zn site, we then examined ZIF-4 ($\text{Zn}[\text{Im}]_2$),^[21] which has two crystallographically non-equivalent Zn sites, to see if these two sites can be differentiated by ^{67}Zn NMR. Figure 1c illustrates ^{67}Zn MAS spectrum of ZIF-4 at 21.1 T. The spectrum can only be simulated by two sites (Figure 1c) and the two

sets of the EFG parameters extracted from the simulations are listed in Table 1. An inspection of the structural data (Table S1) reveals the degrees of distortion in two ZnN_4 tetrahedra is significantly different.^[21] The dispersions of the Zn–N bond lengths and the N–Zn–N bond angles are larger for Zn1 than those for Zn2. Thus, the ^{67}Zn signal with a larger C_Q value is assigned to the Zn1 site. This assignment has been confirmed by the theoretical calculations (see below).

The acquisition times for ^{67}Zn MAS NMR spectra in the above mentioned ZIFs are reasonably short, which were 2h, 1h and 10h for ZIF-8, ZIF-14 and ZIF-4, respectively. Acquiring the spectrum of another ZIF material, ZIF-7 ($\text{Zn}[\text{BIm}]_2$, BIm = benzimidazolate),^[21, 40] however, requires a much longer time. The pattern in the static spectrum recorded for this sample at 21.1 T (Figure 2) is rather broad (~40 kHz), preventing an MAS experiment from being performed with a 7 mm MAS probe used in this work. The static spectrum acquired after 25h still has a rather poor S/N ratio. Considering that this intensity corresponding to a very small amount of ^{67}Zn atoms ($0.1 \text{ }^{67}\text{Zn atoms / nm}^3$)^[21] is spread over 40 kHz range, the low S/N ratio is not surprising. The WURST-QCPMG spectrum of this material was also acquired (not shown). However, the short T_2 precludes any gain in S/N ratio (see *Experimental Section* for more detailed explanations). Nonetheless, the spectrum shown in Figure 2 can be simulated by one Zn site, yielding an estimated $C_Q(^{67}\text{Zn})$ value of 6.2 MHz. The isotropic ^{67}Zn NMR chemical shifts in all four studied ZIF materials were found within 260–320 ppm range, typical for ZnN_4 tetrahedral coordination in other organic solids.^[38]

To better understand the observed ^{67}Zn NMR spectra, *ab initio* computational studies were carried out. The Projector Augmented-Wave (PAW) method implemented in

the CASTEP code has been widely used recently to predict NMR properties in periodic solids.^[43-48] However, the computing power required for the CASTEP calculation increases with increasing unit cell sizes. The unit cells of the MOFs examined in this work are rather large (ranging from 4,300 to 18,700 Å³). The large unit cell volume (hence the number of electronic bands) precludes us from performing CASTEP calculations using the computational resources available to us. Instead, hybrid density functional theory (DFT) method at B3LYP level implemented in Gaussian was used to analyze the experimental results. The cluster approach is computationally more expedient and has been widely and successfully applied to various materials with two- and three-dimensional structures.^[49-54] Four model Zn clusters were constructed from the frameworks of ZIF-8, ZIF-14, ZIF-4 and ZIF-7, to calculate the EFG tensor parameters at their Zn centers (Figure 3). The calculated $C_Q(^{67}\text{Zn})$ values are in a reasonably good agreement with the experimental data (Table 1). It is also worth mentioning that for ZIF-4, the calculations do confirm the assignments proposed earlier, *i.e.*, the observed Zn signal with a larger C_Q indeed originates from Zn site 1.

The above results demonstrated that ^{67}Zn NMR is sensitive to the local Zn structure and that the theoretical calculations can predict NMR parameters reasonably well. The next step is to apply these techniques to an investigation of a more complex material, namely MOF-5 and to try obtaining information about the effect of desolvation on the local Zn environment.

MOF-5 is one of the most widely studied MOF compounds (Figure 4a). It possesses large cubic cavities with oxygen-centered Zn₄O tetrahedra at each of the cube's corners connected by an organic linker, 1,4-benzendicarboxylate (BDC) ligand. It is

thermally stable up to 350°C and has a very large surface area of *ca.* 4,000 m²/g. Previous studies showed that the solvent molecules can be completely removed from the framework by either solvent extraction or heat treatment while the framework still maintains its integrity.^[19, 55, 56] The solvated MOF-5 sample used in this study contains 14.9 % (by weight) of chloroform in its voids.

The ⁶⁷Zn MAS spectrum of solvated MOF-5 is shown in Figure 4b, displaying one resonance which is very narrow (with a FWHH of ~1 kHz). Observation of a single Zn signal is consistent with the crystal structure.^[19] The narrow and relatively symmetric peak in the MAS spectrum is due to the fact that the local environment around Zn is fairly symmetric as shown by the structure. The ⁶⁷Zn MAS spectrum of partially desolvated MOF-5 with *ca.* 8.2 wt.% guest molecules becomes broader (Figure 4b). Similarly, the corresponding ⁶⁷Zn static spectrum is also broader than that of the solvated sample (Figure 4c). For the partially desolvated sample, both MAS and static spectra can be simulated with a single Zn site, yielding a $C_Q(^{67}\text{Zn}) = 3.4(2)$ MHz and $\eta_Q = 0.40(10)$. It is clear that the differences in the spectra between solvated and partially desolvated samples are due to the changes in the Zn coordination environment.

To gain further insight into the relation between the observed ⁶⁷Zn NMR spectra and the possible structural distortions in MOF-5 upon desolvation, the approach of computational modeling was employed. Specifically, we carried out the DFT calculations of the ⁶⁷Zn NMR tensors on a series of Zn₄O(BDC)₆⁶⁻ clusters with slightly modified geometries. Several possible models of distortion were considered: the first model (I) assumes that the core oxygen atom moves upon desolvation along the *C*₂ axis in the cluster (Figure 5a), resulting in two non-equivalent Zn sites with a ratio of 2:2. The

second model (**II**) assumes the core oxygen moving along one of the Zn–O_{core} bond (C_3 axis) directions and such a movement would lead to two non-equivalent Zn sites with a ratio of 1:3 (Figure 5b). The third model (**III**) involves the simultaneous displacement of the Zn atoms coordinated to the same carboxylate group along the Zn–O_{BDC} bond direction (Figure 5c). The last model (**IV**) involves simultaneously changing the O–C–O angle of carboxylate ligand of two opposing BDC groups (Figure 5d). For each model, ^{67}Zn chemical shielding and EFG tensors were calculated and the selected plots of the magnitude of $C_Q(^{67}\text{Zn})$ and the size of chemical shift anisotropy (span, Ω) as a function of the varied structural parameter are illustrated in Figures S2 and S3.

For each model, a series of theoretical MAS and static spectra were calculated by using the computed NMR parameters, which then were compared with the overall profiles of the experimental spectra. Figure 6 illustrates the best-matching MAS and static spectra for each type of distortion (for calculated NMR parameters used in the simulation see Table S2). It appears that the best-matching MAS and static spectra corresponding to a change in O–C–O angle by 4 degrees (model **IV**) have the overall line-shapes more resembling experimental ones than those obtained from other models. The corresponding Zn–O distances and O–Zn–O angles for the Zn site are summarized in Table S3. All these parameters are within the ranges reported for various MOF-5 structures based on crystallographic studies.^[19, 55, 57]

We have also examined ^{67}Zn NMR spectra in a completely desolvated MOF-5 sample. The breadth of the central transition pattern in the static spectrum of this sample is about 45 kHz (Figure 4c), which precludes MAS experiments using the 7 mm MAS probe employed in this work. Although S/N is low, the spectrum can still be fitted

nevertheless with a single Zn site, generating a $C_Q(^{67}\text{Zn})$ of 7.4(5) MHz and η_Q of 0.40(20). The much larger $C_Q(^{67}\text{Zn})$ value suggests that the distortion in the local Zn environment in fully desolvated samples is substantially more significant than in partially desolvated MOF-5. Interestingly, η_Q value remains the same, suggesting that the distortion pathway might remain unchanged. Using the same four distortion models and the procedures described earlier, we also calculated the static spectra as a function of degree of the distortion for each model. Figure S4 displays the best-matching static spectra from each type of distortion. The calculated static spectrum resulting from a change of O–C–O angle (model **IV**) from 125° in solvated to 137° in a fully desolvated sample (corresponding to an increase in the Zn–O_{BDC} distance by 0.11 Å) provides the best match with that observed experimentally. The computed NMR parameters used to calculate the theoretical spectra (shown in Figure S4) are summarized in Table S2. It should be pointed out that the proposed distortions are simplified models and the real situation might be more complicated. Nonetheless, the combination of the ^{67}Zn NMR data and the theoretical calculations does shed light on the desolvation process in MOF-5. Broadening of ^{67}Zn NMR spectra in MOF-5 upon desolvation resembles similar effects observed in ^{27}Al NMR spectra of dehydrated zeolites,^[58, 59] indicating a possible common origin of the broadening in two related families of porous materials.

Finally, using ZIF-8 system as an example, we show that the ^{67}Zn NMR can be used to study the host-guest interaction in MOFs. Figure 7 illustrates ^{67}Zn MAS spectra of a fully desolvated (empty) ZIF-8, the ZIF-8 with benzene molecules trapped inside SOD cages, and the ZIF-8 with internal voids filled with water. The spectrum of the fully desolvated ZIF-8 (Figure 7a) is very narrow, but it does exhibit a typical pattern arising

from quadrupolar coupling interactions. Simulations yielded a $C_Q(^{67}\text{Zn}) = 1.6(2)$ MHz and $\eta_Q = 0.30(10)$. The results indicate that unlike MOF-5, the framework of ZIF-8 appears more rigid^[60] and desolvation via heating does not cause significant changes in the local Zn environment. The pore opening of ZIF-8 (3.4 Å) is too small to directly adsorb benzene. But benzene can be captured in the SOD cage (with a diameter of ~11.6 Å) when it is present in the initial solution prior to crystallization. As shown in Figure 7b, ^{67}Zn MAS spectrum of the ZIF-8 containing captured benzene (16.1 weight percent or ~4 molecules per SOD cage) is very sharp and symmetrical, indicating that the small residual quadrupolar interactions detected in the MAS spectrum of the desolvated ZIF-8 vanishes. Interestingly, the proton-decoupled ^{67}Zn MAS spectra of ZIF-8 loaded with 19.4 weight percent of water as shown in Figure 7c is broader than both those of desolvated and benzene containing ZIF-8. The asymmetric line-shape (which does not correspond to the pure central transition pattern due to quadrupolar interactions) and the fact that the corresponding static spectrum (not shown) is not narrowed significantly by magic-angle spinning suggest that the observed resonance may result from a distribution of chemical shift and/or quadrupolar coupling interactions. This suggests that the variations in the observed ^{67}Zn spectra are due to differences in the distributions of guest molecules.

We have performed a series of classical molecular dynamics (MD) simulations to examine the variations in the guest distributions in ZIF-8, with 17.1% water and 20.0% benzene (by weight). The symmetry of the environment around the zinc is determined from the MD trajectories with a spherical angle distribution function. Angular distributions are calculated for each individual reference atom as the average number

density within a shell of a given radius of the second atom type over the simulation, divided into the series of spherical sectors at incremental angles from a reference vector, see Figure S5. The four tetrahedrally oriented directions of the Zn–N bonds are extracted from the framework positions and used as the reference vectors for the angular distributions. Typical examples of these are shown in Figures 8a and 8b. The difference between the four angular distributions can be quantified by the standard deviation between them and can hence be used as a measure of the change to the spherical symmetry; large deviations between the four distributions indicating that the symmetry is lower and almost identical distributions indicate that the symmetry of the framework is maintained and may be further averaged. To characterize the symmetry for the complete structure the standard deviations between the directions for each zinc atom have been averaged over all the zinc atoms in the simulation supercell.

In our analysis, we calculated the distributions within a 10 Å shell, over 20 ns simulation lengths. Figures 8a and 8b show the four individual angular distributions for a single zinc atom in benzene-loaded and water-loaded ZIF-8. In the benzene loaded case, there is little difference between the distributions; however the symmetry is lost for the water where the distribution seen from each reference vector is completely different, mainly due to the uneven distribution of filled and empty pores. These two examples represent typical cases, and for both systems different reference atoms show a range of variations in distributions. This is shown in the average standard deviation for all atoms in Figure 8c, where one might expect the benzene loaded ZIF-8 to have a lower average if all zinc atoms had an environment the same as this example. However, the standard deviation analysis does show that the spherical symmetry in the benzene-loaded system is

much greater than that in the water loaded system, which accounts for the averaged EFG observed. The effect of the timescale on the distributions is also shown in Figure 8c. The distribution of water does not change on increasing timescales to longer than 1 ns, however the benzene is more evenly distributed if measured over 20 ns than for just 1 ns. This indicates that the benzene, as expected, is less mobile than water, but still has a more even distribution on the longer timescale. There is no further evening of the distribution if the simulation is extended to 40 ns.

Figure 9 shows an overlay of the guest atom positions taken from snapshots every nanosecond during the 20 ns trajectory that further support the conclusions. Qualitatively this shows the water molecules, which can easily diffuse through the channels between pores, conglomerate to form nano-droplets within the pores. This results in some pores completely emptying of water, even when the simulation begins from a homogeneous starting state. Benzene, on the other hand, cannot travel between pores, and there is an even distribution of guests in the pores assumed to be present at the time of synthesis. Moreover, during the MD simulations we also observe a rapid exchange of benzene molecules between the adsorption sites within a pore. This suggests that there is a greater variation in the guest distribution with water compared to benzene. When considering the zinc atoms in these cases, it is clear that the uneven distribution of the water will negate the symmetry of the framework, resulting in a slight distribution of Zn environments and hence the EFGs. For the ZIF-8 loaded with benzene, however, the guest molecules are more evenly distributed between the four reference directions, resulting in an averaging of the EFG interactions giving the narrowed line-shape.^[61]

Conclusion

In conclusion, this work shows that acquiring solid-state ^{67}Zn NMR spectra of Zn-containing MOF-based materials at natural ^{67}Zn abundance is feasible at ultrahigh magnetic field of 21.1 T. ^{67}Zn spectra are sensitive to the local Zn environment and to the presence of guest species. We demonstrate that in combination with computational modeling, ^{67}Zn SSNMR can be used as an effective tool not only for directly probing the local environment of the Zn ions in the framework, but also for investigating host-guest interactions in MOF-based materials. We wish to point out that the feasibility of examining the Zn local structure in MOFs at natural abundance is important since the cost of ^{67}Zn isotopic enrichment is prohibitively high. Since NMR instruments operating at very high magnetic fields are becoming increasingly accessible, it is hoped that this work will encourage other researchers to use ^{67}Zn SSNMR for MOF materials characterization.

Experimental Section

Sample preparation. All the ZIFs and MOF-5 samples were prepared according to the previously reported procedures with some modifications (see *Supporting Information* for details). Powder X-ray diffraction (Figure S6) and ^{13}C CPMAS NMR (Figure S7) experiments were performed to check the identity and purity of all the ZIF samples and they are in good agreement with the literature. Powder X-ray diffraction patterns were recorded with an X-ray diffractometer (Rigaku, MiniFlex II) using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) operating at 30 kV and 15 mA. Scans were acquired between 2.1 and 40° (2θ) at a rate of $4^\circ/\text{min}$.

Solid-state ^{67}Zn NMR. Most ^{67}Zn solid-state NMR experiments were conducted at 21.1 T on a Bruker Avance II spectrometer at the *National Ultrahigh-field NMR Facility for Solids* in Ottawa, Canada (www.nmr900.ca), operating at 56.4 MHz. The samples were ground into a fine powder and then packed into 7 mm o.d. Bruker zirconia rotors inside a glove box with o-ring drive caps. A 7 mm Bruker MAS probe was used for all MAS experiments with a one-pulse sequence under magic-angle spinning rate of 5 kHz. The rotors were spun using dry nitrogen gas. Static ^{67}Zn NMR spectra of as-synthesized ZIF-8, ZIF-7, partially and fully desolvated MOF-5 were acquired with proton decoupling (the decoupling field: ~ 25 kHz) by using the Hahn-echo pulse sequence $[(\pi/2)-\tau-(\pi)-\tau-\text{acq}]$, τ = interpulse delays of 20 - 50 μs on a home-built 7-mm H/X low-gamma NMR probe for stationary samples with a dual resonator design. We also performed ^{67}Zn WURST-QCPMG (Quadrupolar Carr-Purcell-Meiboom-Gill) experiments^[62, 63] on ZIF-8, ZIF-4 and ZIF-7 (data not shown). Unfortunately, the spectra are not very useful. The ZIF samples examined in this study have very short T_2 relaxation times, which results in few echoes in the echo-train, effectively preventing signal enhancement. Furthermore, due to the short T_2 , the echo delays have to be set very short, leading to the large spikelet separation in the spectra after Fourier transformation. Since the most ^{67}Zn NMR spectra of the materials examined in this study are relatively narrow, the powder patterns are only split into very few spikelets. Consequently, the line-shape of the powder pattern cannot be accurately defined. We found that the simple Hahn-echo sequence with short delays and proton decoupling is more suitable for acquiring ^{67}Zn NMR spectra of the MOFs investigated in this particular study than the QCPMG type of

experiments. The detailed spectrometer conditions for each experiment are summarized in Table S4.

For as-synthesized ZIF-8, additional static ^{67}Zn NMR spectra were also recorded with proton decoupling at 9.4 T on a Varian Infinity Plus 400 WB spectrometer [$\nu_0(^{67}\text{Zn}) = 24.9$ MHz] using a 5-mm HFX T3 MAS probe with a Hahn-echo pulse sequence. The relaxation delay used was 1 s. A 1M aqueous $\text{Zn}(\text{NO}_3)_2$ solution was used as a standard for referencing ^{67}Zn chemical shifts ($\delta_{\text{iso}} = 0.0$ ppm) and also for pulse calibration.

NMR spectral simulation. All the NMR parameters, including quadrupolar coupling constant (C_Q), asymmetry parameter (η_Q), isotropic chemical shift (δ_{iso}), span (Ω) and skew (κ) were determined by simulations of the NMR spectra using the WSOLIDS1 (an analytical simulation software package developed by Eichele and Wasylishen).^[64] The error for each measured parameter was determined by visual comparison of experimental spectra with simulations. The parameter of concern was varied bidirectionally, starting from the best-fit value and all other parameters were kept constant, until noticeable differences between the spectra were observed.

DFT calculations. *Ab initio* calculations were conducted using Gaussian 09 program^[65] running on the dual-core 2.6 GHz or quad-core 2.4 GHz Opteron HP workstations with 4 and 32 GB memory, respectively, on SHARCNET (www.sharcnet.ca). The EFG and the chemical shielding (CS) tensors of ^{67}Zn in all the model clusters were calculated using hybrid Density Functional Theory (DFT) at B3LYP level of theory using the GIAO method. The basis sets used were 6-311G* for Zn atoms, 6-311+G* for N or O atoms bonded directly to Zn atoms and 6-31G* for other atoms. The basis sets were chosen based on previous studies, which showed good agreement

with experimental values.^[28, 34, 38] All model clusters for each system were built from the coordinates of their corresponding crystal structures. Some clusters were optimized wherever necessary. The effect of cluster size on the calculated EFG parameters was tested by varying the cluster size for each system. Clusters larger than those reported in this work did not significantly change the EFG parameters. It should be pointed out that the Gaussian program uses its own internal coordinates to calculate NMR properties for non-periodic systems; hence only relative position within the clusters themselves matters. Even so, translations and random reorientations of chosen clusters to different origins with use of internal coordinated disabled (while keeping the same relative positions the same) did not affect the calculated EFG parameters. The EFG tensor components are defined as: $|V_{XX}| \leq |V_{YY}| \leq |V_{ZZ}|$; $C_Q = (eV_{ZZ}Q/h) \times 9.7177 \times 10^{21}$ (Hz); $\eta_Q = (V_{XX} - V_{YY})/V_{ZZ}$, where e is the electric charge; Q is the nuclear quadrupole moment [$Q = 0.150 \times 10^{-28} \text{ m}^2$],^[66] and h is Planck's constant. A conversion factor of $9.7177 \times 10^{21} \text{ V m}^{-2}$ was needed to convert eQV_{ZZ} to C_Q (in Hz) due to V_{ZZ} being calculated in atomic units. The CS tensor components are described by three principal components (δ_{11} , δ_{22} , and δ_{33}) with Herzfeld-Berger convention: $\delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$, $\Omega = \delta_{11} - \delta_{33}$, $\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega$. One of the three Euler angles, β , describes the angle between the two largest components of the EFG and the CS tensors (V_{ZZ} and δ_{33}) ranging from 0 to 180°. The EFG and the CS tensor parameters were extracted from the Gaussian output using the EFGShield program.^[67] Calculated ^{67}Zn isotropic chemical shielding (σ_{iso}) values for all MOF-5 clusters were converted to the corresponding chemical shift (δ_{iso}) values by referencing it to the solvated MOF-5 in order to get the best agreement between calculated and experimental values: $\delta_{\text{iso}} \cong 1772 - \sigma_{\text{iso}}$ (all in ppm), with 1772 ppm

corresponding to the sum of experimental shift value (160 ppm) and calculated shielding value (1612 ppm) of solvated MOF-5.

MD simulations. Molecular dynamics simulations were carried for guest loaded ZIF-8 using classical force-field methods within the DL_POLY simulation package.^[68] Lennard-Jones parameters are taken from the Universal Force Field (UFF)^[69] and combined with Lorentz-Berthelot mixing rules for cross terms. Values for the individual atom types are given in Table S5. Partial atomic charges for Coulombic interactions are given in Table S6. Charges for the ZIF-8 framework were calculated with the REPEAT^[70] method with an electrostatic potential derived from a periodic density functional theory (DFT) calculation using the CPMD software. The DFT calculations used PBE pseudopotentials^[71, 72] and the positions of hydrogen atoms were optimized from the X-ray structure.^[21] Benzene was modeled using a rigid CCSD(T) optimized structure (C–H and C–C bonds of length 1.09 Å and 1.40 Å respectively), point charges fitted with CHELPG in Gaussian 09,^[65] and standard UFF parameters. Water was modeled using the standard TIP5P-Ew model.^[73] The labeling for the unique framework atoms is shown in Figure S8. A fixed 2×2×2 supercell of the framework was used for all simulations. The required number of guest molecules was calculated from the experimentally determined occupancies. The numbers of guests used in the simulations are shown in Table S7. Systems were loaded with the guests initially evenly distributed with equal numbers in each pore (sixteen pores in a 2×2×2 supercell) for the *upper bracket* occupancies. Guests were also removed from the upper bracket configuration to give the *closest approximation*, which gives a less homogeneous initial distribution; however the results for such a system showed no significant difference to the *upper*

bounds case, so we report only those results here. The system was propagated in the NVT ensemble at 298 K with a 1.0 fs time step following 0.1 ns of temperature scaled equilibration. The distribution of guests is calculated over different timescales extracted from the complete simulation.

Acknowledgements. YH and TKW thank NSERC Canada for the Discovery grants. WW and JD gratefully acknowledge the National Natural Science Foundation of China (NSFC) for research grants. Access to the 900 MHz NMR spectrometer was provided by the *National Ultrahigh Field NMR Facility for Solids* (Ottawa, Canada), a national research facility funded by the Canada Foundation for Innovation, the Ontario Innovation Trust, Recherche Québec, the National Research Council Canada, and Bruker BioSpin and managed by the University of Ottawa (<http://www.nmr900.ca>). The computational work was made possible by the facilities of SHARCNET (www.sharcnet.ca).

Supporting Information Available. Supporting information for this article (detailed sample preparation; Figures S1-S8 – additional ^{67}Zn static NMR spectra of as-synthesized ZIF-8 at 9.4 and 21.1 T, plots of ^{67}Zn C_Q and span values as a function of varied structural parameters, comparison between ^{67}Zn experimental and theoretical static NMR spectra of fully desolvated MOF-5 at 21.1 T, schematic of spherical vector used for calculating guest distributions, powder XRD pattern and ^{13}C CPMAS NMR spectra of ZIF samples, atom labeling for ZIF-8; Tables S1-S7 – structural data for ZIF samples, list of calculated ^{67}Zn EFG and CS tensor parameters of MOF-5, list of structural data for

MOF-5 from literature and present work, detailed experimental ^{67}Zn NMR conditions, Lennard-Jones parameters, partial atomic charges for ZIF-8, number of guest molecules in molecular dynamics simulations) is available on the WWW under <http://dx.doi.org/10.1002/chem.201201563>.

References:

- [1] J. R. Long, O. M. Yaghi, *Chem. Soc. Rev.* **2009**, 38, 1201-1508.
- [2] H.-C. Zhou, J. R. Long, O. M. Yaghi, *Chem. Rev.* **2012**, 112, 673-674.
- [3] S. Bordiga, F. Bonino, K. P. Lillerud, C. Lamberti, *Chem. Soc. Rev.* **2010**, 39, 4885-4927.
- [4] R. K. Harris, R. E. Wasylshen, M. J. Duer, *NMR Crystallography*, John Wiley & Sons Ltd, **2009**.
- [5] S. E. Ashbrook, M. E. Smith, *Chem. Soc. Rev.* **2006**, 35, 718-735.
- [6] J. Gonzalez, R. Nandini Devi, D. P. Tunstall, P. A. Cox, P. A. Wright, *Microporous Mesoporous Mater.* **2005**, 84, 97-104.
- [7] S. L. Gould, D. Tranchemontagne, O. M. Yaghi, M. A. Garcia-Garibay, *J. Am. Chem. Soc.* **2008**, 130, 3246-3247.
- [8] D. I. Kolokolov, H. Jovic, A. G. Stepanov, V. Guillermin, T. Devic, C. Serre, G. Ferey, *Angew. Chem., Int. Ed.* **2010**, 49, 4791-4794.
- [9] T. Ueda, K. Kurokawa, H. Omichi, K. Miyakubo, T. Eguchi, *Chem. Phys. Lett.* **2007**, 443, 293-297.
- [10] W. Bohlmann, A. Poppl, M. Sabo, S. Kaskel, *J. Phys. Chem. B* **2006**, 110, 20177-20181.
- [11] K. J. Ooms, R. E. Wasylshen, *Microporous Mesoporous Mater.* **2007**, 103, 341-351.
- [12] M.-A. Springuel-Huet, A. Nossov, Z. Adem, F. Guenneau, C. Volkringer, T. Loiseau, G. Ferey, A. Gedeon, *J. Am. Chem. Soc.* **2010**, 132, 11599-11607.
- [13] Y. Jiang, J. Huang, B. Kasumaj, G. Jeschke, M. Hunger, T. Mallat, A. Baiker, *J. Am. Chem. Soc.* **2009**, 131, 2058-2059.
- [14] M. Muller, S. Hermes, K. Kahler, M. W. E. van den Berg, M. Muhler, R. A. Fischer, *Chem. Mater.* **2008**, 20, 4576-4587.
- [15] A. J. Rossini, A. Zagdoun, M. Lelli, J. Canivet, S. Aguado, O. Ouari, P. Tordo, M. Rosay, W. E. Maas, C. Copéret, D. Farrusseng, L. Emsley, A. Lesage, *Angew. Chem., Int. Ed.* **2012**, 51, 123-127.
- [16] T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, G. Ferey, *Chem.-Eur. J.* **2004**, 10, 1373-1382.
- [17] J. P. S. Mowat, S. R. Miller, A. M. Z. Slawin, V. R. Seymour, S. E. Ashbrook, P. A. Wright, *Microporous Mesoporous Mater.* **2011**, 142, 322-333.
- [18] C. Volkringer, T. Loiseau, G. Ferey, C. M. Morais, F. Taulelle, V. Montouillout, D. Massiot, *Microporous Mesoporous Mater.* **2007**, 105, 111-117.

- [19] H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276-279.
- [20] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469-472.
- [21] K. S. Park, Z. Ni, A. P. Cote, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe, O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 10186-10191.
- [22] A. Phan, C. J. Doonan, F. J. Uribe-Romo, C. B. Knobler, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2010**, *43*, 58-67.
- [23] T. J. Bastow, *J. Phys.: Condens. Matter* **1996**, *8*, 11309-11315.
- [24] G. Wu, S. Kroeker, R. E. Wasylshen, *Inorg. Chem.* **1995**, *34*, 1595-1598.
- [25] A. C. Kunwar, G. L. Turner, E. Oldfield, *J. Magn. Reson.* **1986**, *69*, 124-127.
- [26] G. Wu, *Chem. Phys. Lett.* **1998**, *298*, 375-380.
- [27] S. Sham, G. Wu, *Can. J. Chem.* **1999**, *77*, 1782-1787.
- [28] R. Ida, G. Wu, *J. Phys. Chem. A* **2002**, *106*, 11234-11239.
- [29] A. S. Lipton, M. D. Smith, R. D. Adams, P. D. Ellis, *J. Am. Chem. Soc.* **2002**, *124*, 410-414.
- [30] T. J. Bastow, *Chem. Phys. Lett.* **2003**, *380*, 516-520.
- [31] F. H. Larsen, A. S. Lipton, H. J. Jakobsen, N. C. Nielsen, P. D. Ellis, *J. Am. Chem. Soc.* **1999**, *121*, 3783-3784.
- [32] A. S. Lipton, T. A. Wright, M. K. Bowman, D. L. Reger, P. D. Ellis, *J. Am. Chem. Soc.* **2002**, *124*, 5850-5860.
- [33] A. S. Lipton, C. Bergquist, G. Parkin, P. D. Ellis, *J. Am. Chem. Soc.* **2003**, *125*, 3768-3772.
- [34] Y. Zhang, S. Mukherjee, E. Oldfield, *J. Am. Chem. Soc.* **2005**, *127*, 2370-2371.
- [35] A. S. Lipton, M. M. Morlok, G. Parkin, P. D. Ellis, *Inorg. Chem.* **2008**, *47*, 5184-5189.
- [36] A. S. Lipton, R. W. Heck, M. Hernick, C. A. Fierke, P. D. Ellis, *J. Am. Chem. Soc.* **2008**, *130*, 12671-12679.
- [37] A. S. Lipton, R. W. Heck, P. D. Ellis, *J. Am. Chem. Soc.* **2004**, *126*, 4735-4739.
- [38] K. H. Mroue, W. P. Power, *J. Phys. Chem. A* **2010**, *114*, 324-335.
- [39] M. L. Fuller, *Science* **1929**, *70*, 196-198.
- [40] X. Huang, J. Zhang, X. Chen, *Chin. Sci. Bull.* **2003**, *48*, 1531-1534.
- [41] X.-C. Huang, Y.-Y. Lin, J.-P. Zhang, X.-M. Chen, *Angew. Chem., Int. Ed.* **2006**, *45*, 1557-1559.
- [42] R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Science* **2008**, *319*, 939-943.
- [43] J. M. Griffin, S. Wimperis, A. J. Berry, C. J. Pickard, S. E. Ashbrook, *J. Phys. Chem. C* **2009**, *113*, 465-471.
- [44] L. A. O'Dell, R. W. Schurko, *Phys. Chem. Chem. Phys.* **2009**, *11*, 7069-7077.
- [45] P. J. Pallister, I. L. Moudrakovski, J. A. Ripmeester, *Phys. Chem. Chem. Phys.* **2009**, *11*, 11487-11500.
- [46] J. V. Hanna, K. J. Pike, T. Charpentier, T. F. Kemp, M. E. Smith, B. E. G. Lucier, R. W. Schurko, L. S. Cahill, *Chem.--Eur. J.* **2010**, *16*, 3222-3239.
- [47] V. K. Michaelis, S. Kroeker, *J. Phys. Chem. C* **2010**, *114*, 21736-21744.
- [48] C. M. Widdifield, D. L. Bryce, *J. Phys. Chem. A* **2010**, *114*, 2102-2116.

- [49] L. Peng, Y. Liu, N. Kim, J. E. Readman, C. P. Grey, *Nat. Mater.* **2005**, *4*, 216-219.
- [50] R. P. Chapman, D. L. Bryce, *Phys. Chem. Chem. Phys.* **2007**, *9*, 6219-6230.
- [51] J. Cuny, S. Messaoudi, V. Alonzo, E. Furet, J.-F. Halet, E. Le Fur, S. E. Ashbrook, C. J. Pickard, R. Gautier, L. Le Polles, *J. Comput. Chem.* **2008**, *29*, 2279-2287.
- [52] S. Cadars, D. H. Brouwer, B. F. Chmelka, *Phys. Chem. Chem. Phys.* **2009**, *11*, 1825-1837.
- [53] F. Dogan, K. D. Hammond, G. A. Tompsett, H. Huo, W. C. Conner, S. M. Auerbach, C. P. Grey, *J. Am. Chem. Soc.* **2009**, *131*, 11062-11079.
- [54] N. Feng, A. Zheng, Q. Wang, P. Ren, X. Gao, S.-B. Liu, Z. Shen, T. Chen, F. Deng, *J. Phys. Chem. C* **2011**, *115*, 2709-2719.
- [55] J. Hafizovic, M. Bjorgen, U. Olsbye, P. D. C. Dietzel, S. Bordiga, C. Prestipino, C. Lamberti, K. P. Lillerud, *J. Am. Chem. Soc.* **2007**, *129*, 3612-3620.
- [56] J. Li, S. Cheng, Q. Zhao, P. Long, J. Dong, *Int. J. Hydrogen Energy* **2009**, *34*, 1377-1382.
- [57] H. Kim, H. Chun, G.-H. Kim, H.-S. Lee, K. Kim, *Chem. Commun.* **2006**, 2759-2761.
- [58] A. P. M. Kentgens, D. Iuga, M. Kalwei, H. Koller, *J. Am. Chem. Soc.* **2001**, *123*, 2925-2926.
- [59] J. Jiao, J. Kanellopoulos, W. Wang, S. S. Ray, H. Foerster, D. Freude, M. Hunger, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3221-3226.
- [60] J. C. Tan, T. D. Bennett, A. K. Cheetham, *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 9938-9943.
- [61] R. W. Schurko, S. Wi, L. Frydman, *J. Phys. Chem. A* **2002**, *106*, 51-62.
- [62] F. H. Larsen, H. J. Jakobsen, P. D. Ellis, N. C. Nielsen, *J. Phys. Chem. A* **1997**, *101*, 8597-8606.
- [63] L. A. O'Dell, R. W. Schurko, *Chem. Phys. Lett.* **2008**, *464*, 97-102.
- [64] K. Eichele, R. E. Wasylishen, v. 1.19.15 ed., **2009**.
- [65] M. J. Frisch, Rev. A.1 ed., Gaussian, Inc., Wallingford CT, **2009**.
- [66] P. Pyykko, *Mol. Phys.* **2008**, *106*, 1965-1974.
- [67] S. Adiga, D. Aebi, D. L. Bryce, *Can. J. Chem.* **2007**, *85*, 496-505.
- [68] W. Smith, T. R. Forester, *J. Mol. Graphics* **1996**, *14*, 136-141.
- [69] A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard, W. M. Skiff, *J. Am. Chem. Soc.* **1992**, *114*, 10024-10035.
- [70] C. Campana, B. Mussard, T. K. Woo, *J. Chem. Theory Comput.* **2009**, *5*, 2866-2878.
- [71] S. Goedecker, M. Teter, J. Hutter, *Phys. Rev. B: Condens. Matter* **1996**, *54*, 1703-1710.
- [72] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.
- [73] S. W. Rick, *J. Chem. Phys.* **2004**, *120*, 6085-6093.

FIGURE CAPTIONS:

Figure 1. ^{67}Zn MAS NMR spectra of a) ZIF-8, b) ZIF-14 and c) ZIF-4 at 21.1 T. Asterisks (*) indicate spinning sidebands.

Figure 2. ^{67}Zn static Hahn-echo NMR spectra of ZIF-7 at 21.1 T.

Figure 3. Model clusters of ZIF compounds used in Gaussian calculations.

Figure 4. a) Framework structure of MOF-5. b) Experimental ^{67}Zn MAS NMR spectra of solvated (top) and partially desolvated MOF-5 (bottom) at 21.1 T. c) Experimental and best-fitted ^{67}Zn static NMR spectra of MOF-5 with different degree of solvation at 21.1 T.

Figure 5. Four possible distortion models in $\text{Zn}_4\text{O}(\text{BDC})_6^{6-}$ cluster of MOF-5.

Figure 6. Comparison of ^{67}Zn experimental MAS (a) and static (b) NMR spectra recorded in partially desolvated MOF-5 at 21.1 T and representative theoretical spectra from four distortion models discussed in the text. The best-fit simulated spectra were done using a single Zn site, while the theoretical spectra were calculated using the parameters that result in the best matches to the experimental data (Table S2).

Figure 7. ^{67}Zn MAS NMR spectra recorded at 21.1 T of a) fully desolvated ZIF-8, b) ZIF-8-benzene and c) ZIF-8- H_2O .

Figure 8. (left) Angular distribution of guest molecules about the tetrahedral symmetry directions for a typical zinc atom over 20 ns simulated molecular dynamics in a) benzene-loaded ZIF-8 and b) water-loaded ZIF-8. (right) c) Angular distribution standard deviations averaged over all zinc atoms and shown for different simulation lengths.

Figure 9. Molecular dynamics trajectories. The positions of all guest molecules at 1 ns intervals over the 20 ns simulation are overlayed on the ZIF-8 framework. a) benzene (hydrogen omitted for clarity) shows an even distribution within the pores; b) water evacuates a number of pores leaving an uneven distribution overall, diffusion is also shown through the empty pores.

Table 1. Experimental and calculated ^{67}Zn EFG parameters in ZIF samples.

Compound	$ C_Q $ (MHz) ^a		η_Q ^b		δ_{iso} (ppm)
	experimental	calculated	experimental	calculated	experimental
ZIF-8 (as-synthesized)	1.1(3)	0.2 [*]	0.80(5)	0.00 [*]	300(5)
ZIF-14	2.8(1)	3.4	0.85(5)	0.63	260(5)
ZIF-4 – site Zn1	5.0(2)	5.2	0.25(10)	0.25	315(10)
– site Zn2	3.8(2)	3.9	0.75(10)	0.50	300(10)
ZIF-7	6.2(3)	7.2	0.95(15)	0.78	275(15)
desolvated ZIF-8	1.6(2)	N/A	0.30(10)	N/A	293(5)

The EFG tensor is described by three principal components V_{JJ} ($J=\text{X-Z}$), ordered such that $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$. ^a $C_Q = eQV_{zz}/h$; ^b $\eta_Q = (V_{xx} - V_{yy})/V_{zz}$. ^{*}calculated values with larger uncertainty due to a small EFG.

TOC text

Natural abundance ^{67}Zn solid-state magic-angle spinning (MAS) and static NMR spectra of several representative metal-organic frameworks were acquired at ultrahigh magnetic field strength of 21.1 T. The ^{67}Zn spectra are sensitive to its local environment and can differentiate non-equivalent Zn sites. Combination of ^{67}Zn NMR data and molecular dynamics simulation provides information on the distribution and dynamics of guest species in the framework.

KEYWORDS: zinc-67, solid-state NMR spectroscopy, metal-organic frameworks, desolvation, host-guest systems

Figure 1

Figure 2

a) ZIF-8 cluster
 ZnMIm_4^{2-}

b) ZIF-14 cluster
 ZnEIm_4^{2-}

c) ZIF-4 cluster
 $\text{Zn}_2(\text{Im})_7^{3-}$

d) ZIF-7 cluster
 ZnBIm_4^{2-}

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

a) Benzene

b) Water

Figure 9

^{67}Zn MAS NMR spectra at 21.1 T

TOC Figure

Supporting Information for:

**Characterization of Zn-containing MOFs by Solid-state ^{67}Zn NMR and
Computational Modeling**

Dr. Andre Sutrisno,^a Dr. Victor V. Tersikh,^b Qi Shi,^c Zhengwei Song,^c Prof. Jinxiang Dong,^{c,*} San Yuan Ding,^d Prof. Wei Wang,^{d,*} Bianca R. Provost,^e Dr. Thomas D. Daff,^e Prof. Tom K. Woo^{e,*} and Prof. Yining Huang^{a,*}

Contribution from:

^a*Department of Chemistry, The University of Western Ontario, London, Ontario, Canada, N6A 5B7. Email: yhuang@uwo.ca, Tel: 519-661-2111 x86384.*

^b*Measurement Science and Standards, National Research Council, Ottawa, Ontario, Canada K1A 0R6.*

^c*Research Institute of Special Chemicals, Taiyuan University of Technology, Shanxi, Taiyuan 030024, P.R. China. Email: dongjinxiangwork@hotmail.com*

^d*State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu, 730000, P. R. China. Email: wang_wei@lzu.edu.cn*

^e*Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5 (Canada). Email: Tom.Woo@uottawa.ca*

Experimental Section – Sample Preparation	Page S3
Figure S1. ^{67}Zn static Hahn-echo NMR spectra of as-synthesized ZIF-8 at 9.4 T and 21.1 T.	Page S6
Figure S2. Plots of ^{67}Zn $ C_Q $ values as a function of the varied structural parameter for the four distortion models.	Page S7
Figure S3. Plots of ^{67}Zn span (Ω) values as a function of the varied structural parameter for the four distortion models.	Page S8
Figure S4. Comparison between the ^{67}Zn experimental static spectrum of fully desolvated MOF-5 at 21.1 T and the theoretical spectra from four distortion models.	Page S9
Figure S5. Schematic of spherical sector used for calculating guest distributions.	Page S9
Figure S6. Powder X-ray diffraction patterns of ZIF samples.	Page S10
Figure S7. ^{13}C CPMAS NMR spectra of ZIF samples at 9.4 T.	Page S11
Figure S8. Unique atom labels for ZIF-8 charges.	Page S13
Table S1. Structural data for four ZIF materials investigated in this study.	Page S14
Table S2. ^{67}Zn EFG and CS tensor parameters used to calculate MOF-5 spectra in Figures 6 and S4.	Page S15
Table S3. Structural data for MOF-5 materials from (a) the literature and (b) the computational modeling in the present work.	Page S16
Table S4. Detailed experimental ^{67}Zn solid-state NMR conditions at 21.1 T.	Page S17
Table S5. Lennard-Jones parameters from the UFF and TIP5P-Ew.	Page S18
Table S6. Partial atomic charges for ZIF-8 and benzene.	Page S18
Table S7. Number of guests used in molecular dynamics simulations calculated from experimental occupancies.	Page S19
References	Page S20

Experimental Section – Sample Preparation

ZIF samples.

Zinc acetate dihydrate ($\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, 98.0 %), imidazole (Im), 2-methylimidazole (MIm, 99.0 %), 2-ethylimidazole (EIm), benzimidazole (BIm) and DMF solvent (*N,N*-dimethylformamide, 99.5 %) were used without further purification. All samples used in this study were synthesized according to the previously reported procedures with some modifications.

ZIF-8 (as-synthesized).^[1] $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.11 g, 0.5 mmol) and 2-methylimidazole (0.16 g, 2.0 mmol) were placed in a small teflon cup, which was supported by a teflon holder. Each cup and holder was placed in a Teflon-lined stainless steel autoclave. DMF (2.0 mL) was added to the bottom of each autoclave. The crystallization was then carried out at 150 °C for 24 h. After cooling to room temperature, the solid products were separated by filtration and washed with ethanol. The desolvation of ZIF-8 was carried out by using the following procedure:^[2] The as-synthesized ZIF-8 sample was immersed in methanol at ambient temperatures for 48 h, followed by heating at 200°C for 5-8 h in air to produce an guest-free ZIF-8 framework structure (labeled as desolvated or empty ZIF-8 sample).

ZIF-14.^[3, 4] $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.22 g, 1.0 mmol) and 2-ethylimidazole (0.48 g, 5.0 mmol) were dissolved in DMF (15 mL) in a 30 mL Teflon-lined stainless steel autoclave. The autoclave was then sealed and heated at 120 °C for 72 h. After cooling to room temperature, the solid products were separated by filtration and washed with ethanol.

ZIF-4.^[2] $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.22 g, 1.0 mmol) and imidazole (0.20 g, 3.0 mmol) were dissolved in DMF (15 mL) in a 30 mL Teflon-lined stainless steel autoclave. The autoclave was then sealed and heated at 120 °C for 72 h. After cooling to room temperature, the solid products were separated by filtration and washed with ethanol.

ZIF-7.^[2, 5] $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.22 g, 1.0 mmol) and benzimidazole (0.59 g, 5.0 mmol) were dissolved in DMF (15 mL) in a 30 mL Teflon-lined stainless steel autoclave. The autoclave was then sealed and heated at 120 °C for 72 h. After cooling to room temperature, the solid products were separated by filtration and washed with ethanol.

ZIF-8-benzene.^[2] $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.22 g, 1.0 mmol) and 2-methylimidazole (0.25 g, 3.0 mmol) were dissolved in benzene (15 mL) in a 30 mL Teflon-lined stainless steel autoclave. The autoclave was then sealed and heated at 120 °C for 72 h. After cooling to room temperature, the solid products were separated by filtration and washed with ethanol.

ZIF-8- H_2O .^[1] $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.11 g, 0.5 mmol) and 2-methylimidazole (0.41 g, 5 mmol) were placed in a small teflon cup, which was supported by a teflon holder. Each cup and holder was placed in a Teflon-lined stainless steel autoclave. H_2O (2.0 mL) was added to the bottom of each autoclave. The crystallization was then carried out at 120 °C for 24 h. After cooling to room temperature, the solid products were separated by filtration and washed with distilled water.

MOF-5 samples.

MOF-5 samples were synthesized according to the previously reported procedures^[6] with some modifications. All starting materials and solvents were used without further purification. Terephthalic acid (633 mg, 3.81 mmol) and triethylamine (1.1 mL) were dissolved in DMF (*N,N*-dimethylformamide, 50 mL) and zinc acetate dihydrate ($\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, 2.12 g, 9.66 mmol) was dissolved in DMF (62.5 mL) with stirring. The zinc salt solution was added drop-wise to the organic solution over 15 min, forming a white precipitate. The reaction mixture was stirred for 2.5 hours. The solids were separated by centrifugation and then immersed in DMF (30 mL) overnight. The as-prepared MOF-5 then underwent thorough solvent-exchange by immersing it in CHCl_3 (30 mL) for 7 days (the solvent was refreshed 3 times over this period) to remove DMF and TEA and excess organic linkers if any. The solids were separated by centrifugation again and the product was dried.

The identity and purity of the sample were checked by powder X-ray diffraction and ^{13}C CPMAS NMR (data not shown). The samples were kept in tightly sealed vials. The voids of final solvent-exchanged MOF-5 were filled with chloroform guest molecules (14.9 % by weight as determined by TGA). This sample is hereafter referred to as solvated MOF-5. The desolvation of MOF-5 was carried out by using a recent literature method.^[7] In particular, the fully desolvated MOF-5 sample was prepared by heating the solvated sample at 250°C in an oven for 12 h to produce a guest-free framework structure (labeled as fully desolvated MOF-5). Upon desolvation, the sample was immediately transformed into a glove box for storage. The degree of desolvation was confirmed by TGA (data not shown).

Figure S1. ^{67}Zn static Hahn-echo NMR spectra of as-synthesized ZIF-8 at 9.4 T and 21.1 T.

Figure S2. Plots of ^{67}Zn $|C_Q|$ values as a function of the varied structural parameter for the four distortion models.

Figure S3. Plots of ^{67}Zn span (Ω) values as a function of the varied structural parameter for the four distortion models.

Figure S4. Comparison between the ^{67}Zn experimental static spectrum of fully desolvated MOF-5 at 21.1 T and the theoretical spectra from four distortion models.

Figure S5. Schematic of spherical sector used for calculating guest distributions. The number density is measured in each spherical sector at incremental angles.

Figure S6. Powder X-ray diffraction patterns of ZIF samples.

Figure S7. ^{13}C CPMAS NMR spectra of ZIF samples at 9.4 T. Asterisks (*) indicate spinning sidebands, while the number signs (#) indicate solvent/guest molecule peaks. The assignments of the framework peaks are indicated on the diagrams.

Zoom in of the selected region:

Zoom in of the selected region:

Figure S8. Unique atom labels for ZIF-8 charges.

Table S1-1. Structural data for four ZIF materials investigated in this study.

Compound	Reference	# of Zn sites (site symmetry)	Channel pore size	Space group	Unit cell volume (Å ³)	# of Zn atoms / nm ³	# of Zn-67 atoms / nm ³
1	ZIF-8 PNAS ^[2] ACIE ^[3]	1 (<i>S</i> ₄)	6-ring	<i>I</i> -4 3 <i>m</i> (no. 217)	4,900	2.45 (12 / 4.90 nm ³)	0.1004
2	ZIF-14 ACIE ^[3] Science ^[4]	1 (<i>C</i> ₂)	8-ring	<i>I</i> <i>a</i> -3 <i>d</i> (no. 230)	18,680	2.57 (48 / 18.68 nm ³)	0.1054
3	ZIF-4 PNAS ^[2]	2 (<i>C</i> ₁)	6-ring	<i>P</i> <i>b c a</i> (no. 61)	4,340	3.68 (16 / 4.34 nm ³)	0.1509
4	ZIF-7 PNAS ^[2] CSB ^[5]	1 (<i>C</i> ₁)	6-ring	<i>R</i> -3 (no. 148)	7,210	2.49 (18 / 7.21 nm ³)	0.1021

Table S1-2. Bond distances and angles for four ZIF samples.

Compound	Zn-N bond distances (Å)	Average ± standard deviation (Å)	N-Zn-N bond angles (degrees)	Average ± standard deviation (degrees)
1	ZIF-8 1.987 (×4)	1.987 ± 0	109.3 (×4), 109.8 (×2)	109.5 ± 0.2
2	ZIF-14 2.001 (×2), 2.017 (×2)	2.009 ± 0.009	104.4, 105.6, 111.0 (×2), 112.6 (×2)	109.5 ± 3.6
3	ZIF-4 – site Zn1 1.967, 1.980, 1.992, 1.997 – site Zn2 1.973, 1.979, 1.982, 1.991	1.984 ± 0.013 1.981 ± 0.008	104.1, 109.4, 108.0, 110.6, 110.9, 113.5 105.3, 107.8, 108.9, 110.2, 111.1, 113.3	109.4 ± 3.2 109.4 ± 2.8
4	ZIF-7 1.983, 1.985, 1.995, 2.001	1.991 ± 0.008	103.6, 105.3, 107.7, 111.6, 113.6, 115.2	109.5 ± 4.7

Table S2. ^{67}Zn EFG and CS tensor parameters used to calculate MOF-5 spectra in Figures 6 and S4.

Model	Zn site	$ C_Q $ (MHz) ^a	η_Q^b	δ_{iso} (ppm) ^c	Ω (ppm) ^d	κ^e	β (deg) ^f
<i>best fit</i>	Zn1	3.40	0.40	160	-	-	-
Partially desolvated MOF-5 (see Figure 6)	I	Zn1	3.45	0.02	147	83	0.88
		Zn2	0.64	0.82	164	114	0.95
	II	Zn1	3.40	0.00	144	76	0.96
		Zn2	1.10	0.03	157	100	0.96
	III	Zn1	3.90	0.61	156	96	0.49
		Zn1	3.64	0.44	169	84	0.77
	IV	Zn1	7.40	0.40	-20	-	-
		Zn1	7.61	0.03	127	52	0.63
Fully desolvated MOF-5 (see Figure S4)	I	Zn1	4.82	0.04	182	151	0.82
		Zn1	7.60	0.00	127	44	0.95
	II	Zn1	1.53	1.00	165	116	0.87
		Zn1	7.17	0.34	157	104	0.19
	III	Zn1	7.48	0.62	117	152	0.63
		Zn1	7.48	0.62	117	152	0.63
	IV	Zn1	7.48	0.62	117	152	0.63
		Zn1	7.48	0.62	117	152	0.63

The EFG tensor is described by three principal components V_{JJ} ($J = X-Z$), ordered such that $|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$.

^a $C_Q = eQV_{zz}/h$; ^b $\eta_Q = (V_{XX} - V_{YY})/V_{ZZ}$.

^c $\delta_{\text{iso}} = 1772 - \sigma_{\text{iso}}$ (all in ppm), with 1772 ppm corresponding to the sum of experimental shift value (~ 160 ppm) and calculated shielding value (1612 ppm) of solvated MOF-5.

The chemical shift tensor is described by three principal components (δ_{11} , δ_{22} , δ_{33}) with Herzfeld-Berger convention such that:

^d $\Omega = \delta_{11} - \delta_{33}$; ^e $\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega$.

^f β , is one of the Euler angle, describes the angle between the two largest components of the EFG and the CS tensors (V_{ZZ} and δ_{33}), ranges from 0 to 180°. The other two Euler angles, α and γ , are 0.

Table S3. Structural data for MOF-5 materials from (a) the literature and (b) the computational modeling in the present work.

(a) The structure data from the literature										
Ref.	Guest species	Space group	# of Zn sites - site symmetry	unit cell length (Å)	unit cell vol. (Å ³)	Bond lengths (Å)		Bond angles (degrees)		
						Zn-O _{core} (O1)	Zn-O _{BDC} (O2)	O1-Zn-O2	O2-Zn-O2	
Nature 1999 ^[8]	C ₆ H ₅ Cl-DMF	<i>F m -3 m</i> (cubic)	1 (<i>C</i> _{3v})	a = 25.669	16,913	1.934	1.911 × 3	112.43 × 3	106.36 × 3	125.02 × 6
	optimized structure					1.990	1.976 × 3	110.49 × 3	108.43 × 3	123.74 × 6
	desolvated	<i>F m -3 m</i> (cubic)	1 (<i>C</i> _{3v})	a = 25.885	17,343	1.950	1.937 × 3	111.28 × 3	107.62 × 3	125.90 × 6
Chem. Comm. 2006 ^[9]	ferrocene	<i>P a -3</i> (cubic)	2 Zn1 (<i>C</i> ₁) Zn2 (<i>C</i> ₃)	a = 25.507	16,595	1.953	1.937, 1.944, 1.970	108.45, 111.84, 113.39	100.95, 108.77, 113.35	126.33 × 3
						1.936	1.928 × 3	111.56 × 3	107.30 × 3	125.22 × 3
JACS 2007 ^[10]	TEA-DMF	<i>R -3 m</i> (trigonal)	2 Zn1 (<i>C</i> _s) Zn2 (<i>C</i> _{3v})	a = 18.41; c = 44.75	13,129	1.924	1.898 × 2, 1.943	111.19, 111.24, 114.35	106.28 × 2, 107.07	121.63 × 3
						2.033	1.924 × 3	111.79 × 3	107.07 × 3	125.83 × 3
(b) The structure data from computational modeling (present work)										
Model IV	Partially desolvated		Zn1			1.934	1.911 × 2, 1.877	111.50, 112.43 × 2	106.36, 106.87 × 2	121 × 2, 125.02 × 4
	Fully desolvated		Zn1			1.934	1.911 × 2, 2.021	112.43 × 2, 114.76	105.06 × 2, 106.36	125.02 × 4, 137 × 2

Table S4. Detailed experimental ^{67}Zn solid-state NMR conditions at 21.1 T.

Sample	Type of experiment	90° pulse length (μs)	SW (kHz)	recycle delay (s)	τ_a (μs)	M (# of loops)	τ_1 (μs)	τ_2 (μs)	τ_3 (μs)	τ_4 (μs)	# scans
ZIF-8 (as-synthesized)	MAS 5 kHz	2	50	1	--	--	--	--	--	--	8192
	static Hahn-echo	4	500	1	--	--	94	--	--	--	8192
	static Hahn-echo (9.4 T)	2.3	50	1	--	--	45	--	--	--	71136
ZIF-14	MAS 5 kHz	1.5	50	1	--	--	--	--	--	--	4096
ZIF-4	MAS 5 kHz	1.5	50	1	--	--	--	--	--	--	36032
ZIF-7	static Hahn-echo	4	100	1	--	--	195	--	--	--	92160
Solvated MOF-5	MAS at 5 kHz	3	50	1	--	--	--	--	--	--	7080
	static WURST-QCPMG	50	200	1	500	32	59	60	60	60	12120
Partially desolvated MOF-5	MAS at 5 kHz	3	50	1	--	--	--	--	--	--	8192
	static Hahn-echo	4	200	1	--	--	94	--	--	--	122880
Fully desolvated MOF-5	static Hahn-echo	4	200	1	--	--	94	--	--	--	61440
desolvated ZIF-8	MAS at 5 kHz	2	50	1	--	--	--	--	--	--	8192
ZIF-8-benzene	MAS at 5 kHz	2	50	1	--	--	--	--	--	--	8192
ZIF-8-H ₂ O	MAS at 5 kHz	2	50	1	--	--	--	--	--	--	8192

Table S5. Lennard-Jones parameters from the UFF and TIP5P-Ew.

Atomic type	$\epsilon / \text{kcal mol}^{-1}$	$\sigma / \text{\AA}$
C	3.4309	0.105
H	2.5711	0.044
Zn	2.4616	0.124
N	3.2607	0.069
O (H ₂ O)	3.0970	0.178

Table S6. Partial atomic charges for ZIF-8 (REPEAT method) and benzene (CHELPG).

Atom identifier	q / e
Zn	0.645
C1	0.397
C2	-0.201
C3	-0.519
N	-0.250
H1	0.155
H2	0.133
C (C ₆ H ₆)	-0.103
H (C ₆ H ₆)	0.103

Table S7. Number of guests used in molecular dynamics simulations calculated from experimental occupancies.

	Water	Benzene	Benzene/Water
Experimental weight %	19.4	16.1	7.8
Experimental guests per pore	18.2	3.7	7.8
Target guests in supercell	291.2	59.2	124.8
<i>Upper bracket</i> guests per pore	19	4	8
<i>Upper bracket</i> guests in supercell	304	64	128
<i>Closest approximation</i> guests in supercell	291	59	125

References:

- [1] Q. Shi, Z. Chen, Z. Song, J. Li, J. Dong, *Angew. Chem., Int. Ed.* **2011**, *50*, 672-675.
- [2] K. S. Park, Z. Ni, A. P. Cote, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe, O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 10186-10191.
- [3] X.-C. Huang, Y.-Y. Lin, J.-P. Zhang, X.-M. Chen, *Angew. Chem., Int. Ed.* **2006**, *45*, 1557-1559.
- [4] R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Science* **2008**, *319*, 939-943.
- [5] X. Huang, J. Zhang, X. Chen, *Chin. Sci. Bull.* **2003**, *48*, 1531-1534.
- [6] D. J. Tranchemontagne, J. R. Hunt, O. M. Yaghi, *Tetrahedron* **2008**, *64*, 8553-8557.
- [7] J. Li, S. Cheng, Q. Zhao, P. Long, J. Dong, *Int. J. Hydrogen Energy* **2009**, *34*, 1377-1382.
- [8] H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276-279.
- [9] H. Kim, H. Chun, G.-H. Kim, H.-S. Lee, K. Kim, *Chem. Commun.* **2006**, 2759-2761.
- [10] J. Hafizovic, M. Bjorgen, U. Olsbye, P. D. C. Dietzel, S. Bordiga, C. Prestipino, C. Lamberti, K. P. Lillerud, *J. Am. Chem. Soc.* **2007**, *129*, 3612-3620.