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New insights into solvent-induced structural changes of ^{13}C labelled metal–organic frameworks by solid state NMR†

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Selective ^{13}C-labelling of carboxylate carbons in the linker molecules of flexible metal–organic frameworks (MOFs) makes solid-state NMR spectroscopy very powerful to investigate solvent-induced local structural changes as demonstrated by ^{13}C and ^{1}H NMR spectroscopy on the pillared layer MOF DUT-8(Ni). Selective identification of polar solvent–node interactions becomes feasible.

Metal–organic frameworks (MOFs) are versatile materials of exceptional porosity[1,2] and promising for applications in gas and liquid phase adsorption, gas storage, separation processes, catalysis, and sensing.[3–6] The framework crystal structure is usually determined by X-ray or neutron diffraction. In contrast, defects, linker disorder, as well as disordered guest molecules and their interactions with the framework are often difficult to study by diffraction techniques. Recently, Yaghi and co-workers demonstrated the impact of disordered solvent molecules on crystallographic experiments illustrating the need for extended analysis of the solvents present within the pores of MOFs.[7] Solvents play a key role for MOFs. They are important for cluster formation and crystallisation in solvothermal syntheses,[8] for solvent exchange to remove side products and unreacted starting materials, solvent removal to obtain guest-free porosity,[9,10] and finally for filling the pores with fluids[11,12] in various applications. In most cases, solvents have only minor influence upon the structure of the framework (rigid MOFs). However, flexible MOFs can undergo massive changes of structure and unit cell volume in response to the adsorption of certain guest molecules.[13] In some cases, specific interactions of solvent molecules with flexible

frameworks are found to dictate the structural response.[14–16] Selective recognition of solvents with different polarity and chemical constitution was recently reported for DUT-8(Ni) with potential sensing applications.[17] However, selective adsorption and guest recognition in flexible MOFs are not fully understood yet. Further in-depth investigations are necessary.

NMR is widely used to study MOFs and their host–guest interactions with adsorbed species by probing either the host or the guest molecules.[18–31] Sensitivity is often a major limitation of NMR spectroscopy, especially for nuclei with low natural abundance like [13]C. Isotope enrichment is then highly desirable. In the present contribution, we describe the application of solid-state NMR to study the interaction of various organic solvent molecules with the flexible MOF DUT-8(Ni)[32] ($Ni_2(2,6\text{-}ndc)_2(dabco)$ (2,6ndc = 2,6-naphthalene-dicarboxylate, dabco = 1,4-diazabicyclo[2.2.2]octane)) to analyse structural changes and underlying, potentially selective host–guest interactions. Solvothermally synthetized DUT-8(Ni) crystals with sizes beyond 1 µm (compound **1**) undergo a pronounced structural transformation during desolvation. The framework switches from an open pore (op) to a closed pore (cp) phase. The structure is re-opened by adsorption of appropriate gases or liquids, resulting in a "gate-opening behaviour". The flexibility of **1** was characterized from a fundamental point of view in several studies.[22,32–40] In contrast, DUT-8(Ni) with crystal sizes below 1 µm, further denoted as compound **2**, is rigid and remains in a metastable open pore phase even after guest removal (Fig. S1–S3, ESI†).[22,36]

[13]C cross polarisation magic angle spinning (CP MAS) NMR spectra of DUT-8(Ni) without isotope enrichment exhibit low intensity especially for non-protonated linker carboxylate carbon atoms.[22,33] Thus, the experiments are very time-consuming and the resulting spectra of low quality. To enhance the sensitivity, carbon atoms of the carboxyl groups of 2,6-H_2ndc were selectively labelled with ^{13}C by lithiation of 2,6-dibromonaphthalene and subsequent carboxylation with ^{13}C-enriched CO_2 (Scheme 1, for details see Section 4 of ESI,† Fig. S4–S6). Because many MOFs are based on linkers containing carboxylic acids,[41] this synthetic

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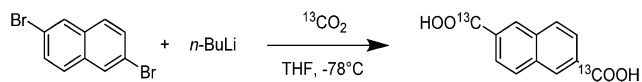 *E-mail: eike.brunner@tu-dresden.de*

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Scheme 1 Reaction scheme of the ^{13}C-labelling of 2,6-dibromo-naphthalene by lithiation and subsequent carboxylation with ^{13}C-enriched CO_2.

approach can be widely applied to provide a strong and selective sensitivity enhancement for solid-state ^{13}C NMR experiments.

Fig. 1 shows the ^{13}C (^1H) CP MAS NMR spectra of 2,6-H_2ndc with selectively ^{13}C-enriched carboxylic acid functionalities and of as made flexible DUT-8(Ni) solvothermally synthesized in *N,N*-dimethylformamide (DMF) (compound **1**). Remarkably, linker incorporation into the MOF lattice causes a huge increase of the isotropic ^{13}C NMR chemical shift from 173 ppm to 269 ppm and of the static linewidth as reflected by the broad spinning sideband pattern. Second moments, M_2, are frequently used measures for line broadening. They can be calculated from the spinning sideband intensities (Fig. S8 and S9, ESI†). An increase of M_2 from 2×10^9 s^{-2} for the pure linker to 2×10^{10} s^{-2} for DUT-8(Ni) occurs at a field corresponding to 800 MHz ^1H resonance frequency. This may be due to two different reasons: (i) an increase of the chemical shift anisotropy due to the coordination of the carboxylate groups to the Ni_2 cluster (Fig. 1) and/or (ii) a paramagnetic broadening due to the neighbouring nickel atoms. For both interactions, M_2 should exhibit a field dependence proportional to the square of the static magnetic field, B_0, of the spectrometer as is indeed observed (Fig. S9, ESI†).[42–45] In contrast, dipolar interactions can be excluded as dominating source of line broadening because the second moment should then be independent of B_0. The remarkably high isotropic ^{13}C NMR chemical shift of 269 ppm points towards a possible paramagnetic shift of the signal due the neighbouring Ni_2 sites. Earlier magnetisation measurements[32] indeed show a paramagnetic susceptibility which is, however, lower than for typical paramagnetic compounds (ESI,† page 11).
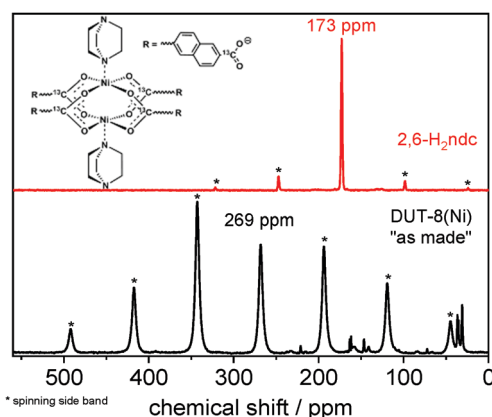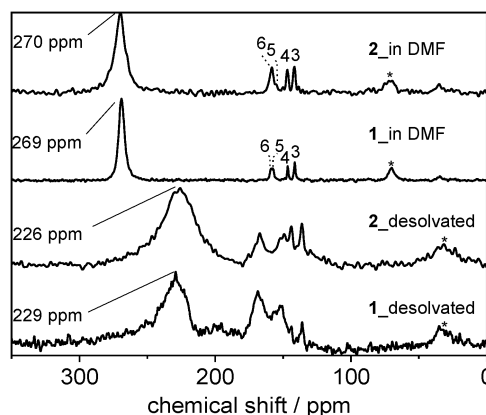
Furthermore, the removal of the solvent from compound **1** leads to structure closing accompanied by an increase of the magnetic susceptibility by a factor of about four.[32] If paramagnetism would have a major effect upon the isotropic chemical shift, solvent removal should result in a further chemical shift increase. The opposite is true, solvent removal reduces the chemical shift to 229 ppm for the carboxylates. Paramagnetic effects can thus not be the dominating source of the high isotropic chemical shift in the as made samples. This conclusion is supported by the absence of EPR signals,[35,40] calculations[46] predicting an antiferromagnetic coupling in the Ni_2 cluster, and the temperature dependence of the carboxylate ^{13}C NMR signal (Fig. S10, ESI†).

Comparison of the spectra for the flexible compound **1** and the rigid compound **2** reveals that the ^{13}C NMR spectra of both materials exhibit very similar chemical shifts. This is true for the as made and the desolvated state (Fig. 2). The fact, that desolvated **2** (op form) exhibits almost the same chemical shift as desolvated **1** (cp form) reveals that the solvent-induced structural transition of compound **1** does not significantly influence the isotropic chemical shift of linker carboxylate groups. Furthermore, the residual linewidth of the ^{13}C CP MAS NMR signal of the linker carboxylates is significantly larger for as made compound **2** compared to **1** (Fig. S11, ESI†). This can be ascribed to a higher degree of linker disorder for compound **2** in agreement with previous observations and may explain the fact that compound **2** is non-flexible, *i.e.*, unable to undergo the structural transition observed in **1** after solvent removal.[22]

To further elucidate the reason for the large isotropic chemical shift of the as made, DMF-containing samples and its decrease during solvent removal, we systematically varied the solvent. A clear correlation between solvent polarity and isotropic ^{13}C chemical shift of the carboxylates is observed (Fig. 3, Table S4 and Fig. S12, ESI†). Note that the open pore state of DUT-8(Ni) filled with nonpolar solvents like *n*-alkanes exhibits practically the same isotropic chemical shift of *ca.* 230 ppm as the closed, solvent-free sample (Fig. 3 and Fig. S12, ESI†).

Fig. 1 ^{13}C CP MAS NMR spectra of 2,6-H_2ndc with selectively ^{13}C-labelled carboxylate groups and of 1 containing 2,6-ndc with selectively ^{13}C-labelled carboxylates measured in DMF. Complete signal assignment is provided in Fig. S7, ESI.† The measurements were carried out at a magnetic field corresponding to 800 MHz ^1H resonance frequency.

Fig. 2 ^{13}C CP MAS NMR spectra of 1 and 2 containing 2,6-ndc with selectively ^{13}C-labelled carboxylates in the solvated (DMF) and solvent free (desolvated) state. Signal assignment is provided in Fig. S7, ESI.†
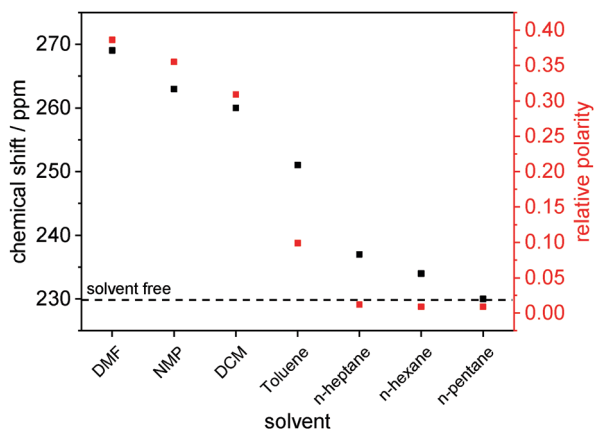
Fig. 3 ^{13}C NMR chemical shift of the carboxylate groups measured for **1** containing different solvents in the pores (NMP: *N*-methyl-2-pyrrolidone; DMF: *N*,*N*-dimethylformamide; DCM: dichloromethane). The relative polarity of the used solvents (*cf.* Table S4, ESI†) is shown in red.

More polar solvents like DMF give rise to a chemical shift change up to *ca.* 40 ppm relative to the latter value.

Potentially, this indicates a specific interaction of the solvent molecules with the paddle wheel units. This hypothesis is further corroborated by ^{1}H MAS NMR studies (*cf.* Fig. 4 and Section 7, ESI† with Fig. S13–S15). A broad signal centred at about 8 ppm occurs for the closed, solvent-free form of **1** due to ^{1}H nuclei located at the aromatic linkers. Moreover, the ^{1}H nuclei of the dabco molecules also contribute to this signal. It is remarkable that the ^{1}H signals of CH$_2$ groups in dabco molecules occur at only *ca.* 3.5 ppm in solution. Solvating **1** with nonpolar solvents like *n*-heptane results in a decent shift of the broad signal to about 9–10 ppm. However, an additional signal at *ca.* 12–13 ppm occurs for the polar solvents DMF, *N*-methyl-2-pyrrolidone (NMP) and dichloromethane (DCM). Using samples containing deuterated linker and/or dabco molecules (compounds **3**, **4**, **5**, for details see Section S1 and Table S1, ESI†), we could assign this additional signal to CH$_2$ groups of dabco molecules (see ESI,†
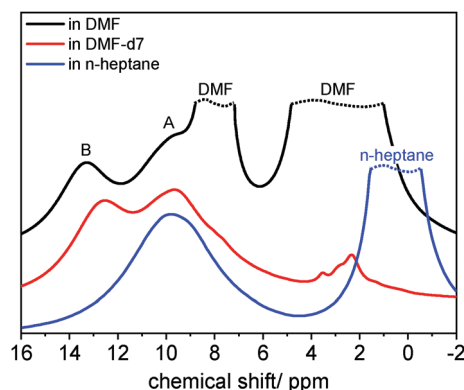

Fig. 4 ^{1}H MAS NMR spectra of **1** loaded with DMF and *n*-heptane. The exchange of DMF by deuterated DMF reveals the two major signals, A and B, belonging to the MOF structure in samples loaded with polar solvents. Minor signals at 2–4 ppm for the sample exchanged with DMF-d7 are due to residual amounts of protonated DMF.

Section 7 and Fig. S13). This assignment is confirmed by the 2D [1]H-^{13}C-HETCOR spectrum, which shows a cross polarisation between the CH$_2$ carbon atom of dabco at *ca.* 35 ppm and ^{1}H nuclei at *ca.* 13 ppm for DMF and 10 ppm for *n*-heptane loaded samples at short mixing times (Fig. S16, ESI†). Relatively high ^{1}H NMR chemical shifts are often considered as indication for hydrogen bond formation.[47] This unexpected observation points towards a specific interaction of polar solvent molecules with the pillaring dabco molecules in DUT-8(Ni). Previous observations suggesting the formation of specific adsorption complexes in the neighbourhood of metal sites in MOFs support this idea.[48,49] Former studies on DUT-8(Ni) showed distinct differences in the adsorption behaviour of aprotic polar and protic polar solvents like alcohols.[17] To investigate the influence of solvent molecules that can act as donor and acceptor (amphiprotic behaviour), we performed a series of experiments with various alcohols. Surprisingly, we could not find a direct correlation between the polarity of the alcohols and the chemical shift in the ^{13}C spectra (Fig. S17, ESI†). The chemical shift decreases from 249 ppm (ethanol) to 242 ppm (propanol) indicating a different inter-action with the framework. The chemical shift then increases with further increasing size of the alcohol up to 254 ppm for octanol – well below the high shift value of *ca.* 270 ppm observed, *e.g.*, for DMF (Fig. 3). Alcohols are amphiprotic, but act more as proton donor than acceptor sites resulting in weaker interactions with the framework. This agrees with previous observations showing that adsorption of alcohols cannot trigger the structural transformation of the desolvated flexible compound **1**.[17] Further investigations are necessary in order to clarify the special behaviour of alcohols.

In summary, we report selective ^{13}C-labelling of the carboxylate group of the 2,6-H$_2$ndc linker used in DUT-8(Ni). This technique provides excellent sensitivity for selectively investigating local structural changes of the nodes of flexible MOFs. Solvent polarity exerts a pronounced influence upon the chemical shift. Nonpolar solvents exhibit weaker interactions with the nodes of the framework. Polar solvents strongly interact with the framework clusters and give rise to substantial shifts of the carboxylate ^{13}C NMR signals. Furthermore, the protons of dabco exhibit a surprisingly high chemical shift depending on solvent polarity, possibly by hydrogen bond formation involving dabco molecules. In addition, the fact that large crystallites of DUT-8(Ni) are flexible in contrast to small crystallites does not originate from different solid-fluid inter-actions as could be derived from the identity of the spectro-scopic signatures for both structural variants. Only one difference between the flexible and rigid variant was detected by ^{13}C NMR spectroscopy: the residual line width of the carboxylate ^{13}C CP MAS NMR signal of the rigid compound **2** is considerably higher than for the flexible compound **1**. Based on the isotope-labelling scheme proposed here, future spectroscopic investigations will enable the in-depth analysis of site-specific host–guest interac-tions and complexes formed by the adsorption of polar solvents in MOFs. This could open up prospects for selectively tuning the adsorption properties by rational materials design towards enhanced selectivity.

Conflicts of interest

There are no conflicts to declare.

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