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Metal–Organic Frameworks

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Dynamics of Benzene Rings in MIL-53(Cr) and MIL-47(V) Frameworks Studied by ^{2}H NMR Spectroscopy[**]

Daniil I. Kolokolov, Hervé Jobic,[*] Alexander G. Stepanov, Vincent Guillerm, Thomas Devic, Christian Serre, and Gérard Férey

Metal–organic frameworks (MOFs) combine metal oxide clusters and organic linkers in almost infinite manners.[1–4] Because the variability in pore dimensions and chemical composition is larger than in zeolites, this class of hybrid porous solids has major potential applications in the fields of adsorption or separation of gases and liquids, catalysis, drug delivery, and others.[4,5] A remarkable feature of some MOFs is their flexibility. The MIL-53 type (MIL: Materials of Institut Lavoisier) is one of the best representatives of the "breathing" MOFs.[6] This series of metal(III) terephthalates of formula ($M^{III}(OH){\cdot}O_2CC_6H_4CO_2$) ($M = Al$, Cr, Fe, Ga), is built up from chains of metal-centered octahedra sharing OH vertices, which are linked in the two other directions by terephthalate groups to create one-dimensional (1D) lozenge-shaped tunnels. Depending on the guest entrapped in the pores, MIL-53(Cr) has been shown to exhibit different crystalline states, corresponding to different pore openings, while the framework topology remains unchanged.[7] The as-synthesized form contains disordered terephthalic acid molecules in the pores and has a cell volume of 1440 $Å^3$. Upon calcination, the free acid is removed and the cell volume increases to 1486 $Å^3$, while it decreases to 1012 $Å^3$ on hydration. This transition between large-pore (LP) and narrow-pore (NP) forms corresponding to anhydrous and hydrated states, respectively, is reversible. On the other hand, MIL-47(V), which is isostructural to MIL-53-LP but without the OH groups, has a rigid framework.[6,8] As a consequence, MIL-47(V) exhibits only type I adsorption isotherms, as expected for gas adsorption in a rigid nanoporous material.

In contrast, steps in the adsorption isotherms of CO_2 and various hydrocarbons occur in MIL-53(Cr) at room temperature, and are associated with two consecutive structural transitions. The transition from the LP to the NP form is observed at low concentration, and the NP-to-LP transition at higher loadings. The structural switching were evidenced by X-ray powder diffraction, adsorption microcalorimetry, and simulations.[9,10] This phenomenon is guest-dependent; for example, MIL-53(Cr) behaves as a rigid framework (LP form) on adsorption of certain small species (H_2 and CH_4), but is flexible for others (Xe).[11] The magnitude of breathing can be related to the van der Waals volume of the guest molecule: the smaller the molecule the more MIL-53(Cr) is able to breathe.[9,11] The largest amplitude of breathing (ca. 40%) is obtained for the empty material.[12]

Surprisingly, the LP–NP transition can occur without any guest, simply by changing the temperature.[12] This conclusion was drawn from elastic and inelastic neutron scattering measurements, which also showed the existence of a large temperature hysteresis in MIL-53(Al). It was suggested that the low-energy librational modes of the aromatic ring are coupled to the structural transition.[12] In MOF-5, the softest twisting or torsional modes of benzene were calculated at similar energies.[13–15] Although the energy of these modes is very low (20–80 cm^{-1}), no rotation of benzene was observed by quasi-elastic neutron scattering (QENS),[13] the timescale of which ranges typically between 10^{-13} and 10^{-8} s.[16] The energy barrier for 180° (π) flips was indeed found to be relatively large, with estimates varying between 51.8[13] and 63 $kJ\,mol^{-1}$.[14] On the longer timescale of ^{2}H NMR spectroscopy ($>10^{-7}$ s), the benzene rings in MOF-5 were found to be stationary at temperatures below 298 K, but π flips were observed at higher temperatures, and all benzene rings execute this motion at 373 K.[17] More recently, an activation energy of 47.3 $kJ\,mol^{-1}$ was obtained for the π-flip rate constant in MOF-5.[18]

In MIL-47 and MIL-53 frameworks, which have 1D pore systems, the dynamics of the benzene rings could more strongly influence the adsorption and transport properties compared to a MOF with 3D pore connectivity. For small molecules, 1D diffusion has been evidenced in MIL-47(V) and MIL-53(Cr) by QENS.[19–21] Moreover, in molecular simulations of these two MILs, the framework was taken to be rigid, and no switching of molecules from one channel to another was observed.[19–21] On a much longer timescale, which is relevant for macroscopic measurements, the rotational motion of benzene could play a role. We used solid-state ^{2}H NMR to determine the flipping rate of benzene rings in MIL-47(V) and MIL-53(Cr) frameworks. An additional

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[*] D. I. Kolokolov, Dr. H. Jobic
Université Lyon 1, CNRS, UMR 5256, IRCELYON, Institut de Recherches sur la Catalyse et l'Environnement de LYON
2. Av. A. Einstein, 69626 Villeurbanne (France)
E-mail: herve.jobic@ircelyon.univ-lyon1.fr

D. I. Kolokolov, Dr. A. G. Stepanov
Boreskov Institute of Catalysis
Siberian Branch of Russian Academy of Sciences
Prospekt Akademika Lavrentieva 5, Novosibirsk 630090 (Russia)

V. Guillerm, Dr. T. Devic, Dr. C. Serre, Prof. G. Férey
Institut Lavoisier, UMR CNRS 8180
Université de Versailles Saint-Quentin-en-Yvelines
78035 Versailles Cedex (France)

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aim is to find out whether the rigidity of MIL-47 and flexibility of MIL-53 are reflected in the dynamics of the organic linkers.

Solid-state ^{2}H NMR experiments were performed at 61.432 MHz on a Bruker Advance-400 spectrometer, by using a high-power probe with 5 mm horizontal solenoid coil. Activated MIL-47(V) and MIL-53(Cr) samples with deuterated aromatic rings were studied, whereby MIL-53(Cr) was initially in the LP form. The paramagnetic metal centers in the two MIL structures (MIL 47: V^{4+}, $S = 1/2$; MIL 53: Cr^{3+}, $S = 3/2$) may influence the ^{2}H NMR spectrum by large frequency shifts and fast relaxation of the nuclear spin.[22] The usual solid echo pulse sequence is not able to compensate these effects and correctly refocus the ^{2}H NMR spectrum, so an Exorcycled quadrupole-echo sequence (90_X–τ_1–90_ϕ–τ_2–Acq–t) was used,[23] where $\tau_1 = 20$ ms, $\tau_2 = 22$ ms, and t is a repetition time for the sequence during accumulation of the NMR signal. The duration of the 90° pulses was 3.0–3.7 µs. The measurements were performed over a broad temperature range, from 103 to 503 K.

To derive information on the dynamics of the aromatic rings, experimental ^{2}H NMR spectra were fitted separately at each temperature according to a dynamical model and to the local geometry. The simulated spectra are obtained by Fourier transform of the powder-average of the quadrupole-echo signal $G(t,\theta,\phi)$ [Eq. (1)][22,24]

$$G(t,\theta,\varphi) = \mathbf{l}\exp(\mathbf{A}t)\exp(\mathbf{A}\tau)\exp(\mathbf{A}^*\tau)\mathbf{P} \tag{1}$$

where **A** is a matrix composed as follows [Eq. (2)]

$$\begin{cases} a_{ii} = i\omega_i - k_{ii} - R^i_{2\mathrm{par}} \\ a_{ij} = k_{ij} \end{cases} \quad \text{with } k_{ii} = \sum_{j\neq i} k_{ij} \tag{2}$$

l is a vector (1,1,…N), where N is the number of sites, **P** a vector of equilibrium population of each site, k_{ij} the exchange rate between sites i and j, $\omega_i(\theta,\phi)$ the ^{2}H NMR frequency at the i-th site, which includes contributions from the pure nuclear quadrupole interaction (ω_{Qi}) and the sum of dipolar interactions between the i-th ^{2}H nucleus and neighboring paramagnetic ions ($\sum \omega_{\mathrm{P}ik}$). The relaxation term of these dipolar interactions is $^kR^i_{2\mathrm{par}}$.

For the two MILs, Figure 1 shows that it is not possible to fit correctly the ^{2}H NMR spectra without taking into account the presence of paramagnetic ions (see also Figures S1 and S2, Supporting Information):

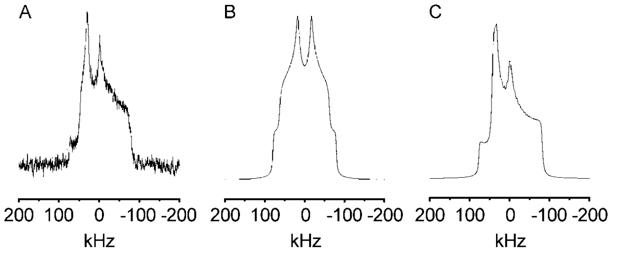

Figure 1. ^{2}H NMR spectra of MIL-53(Cr) at $T = 483$ K. A) Experimental. B) Simulated without any paramagnetic influence. C) Simulated after taking into account the eight nearest ions.

In the final simulations for MIL-47(V) and MIL-53(Cr)-LP, it was sufficient to consider the eight nearest cations (see Figure 2). The strength of interaction with paramagnetic ions is proportional to their total electron spin and rapidly increases for shorter distances (~$1/r^3$). The geometrical parameters (Euler angles and distances) were taken from crystallographic data.[7,8] Apart from the spin state, the dipolar interaction depends on the g tensor, which characterizes the electronic structure of the paramagnetic center. Since the paramagnetic centers are represented by a high-symmetry octahedral ligand field, the g tensor was assumed to be axial with its ZZ main component along the O-M-O direction (M = V, Cr). Its orientation was again derived from the geometry of the material (Figure 2). To obtain the values of the principal components of the tensor, additional ESR measurements were performed in a broad temperature range (from 90 to 473 K). For both MILs, ESR spectra gave a single resonance line with an effective isotropic component $g_{\mathrm{iso}} = 2$. Such values were already reported in the original magnetic susceptibility studies;[7,8] the two MILs have a prominent magnetic characteristic due to the relatively high temperature of phase transitions to the antiferromagnetic state. Fitting of the experimental ^{2}H NMR spectra showed agreement with the ESR measurements and allowed complete characterization of the g tensor: in MIL-47(V) the tensor was found to be almost spherical ($g_{xx} = g_{yy} = \sqrt{3.8}$, $g_{zz} = \sqrt{4.4}$), $g_{\mathrm{iso}} = 2$); MIL-53(Cr) showed stronger anisotropy: ($g_{xx} = g_{yy} = \sqrt{3.2}$, $g_{zz} = \sqrt{5.6}$), $g_{\mathrm{iso}} = 2$).

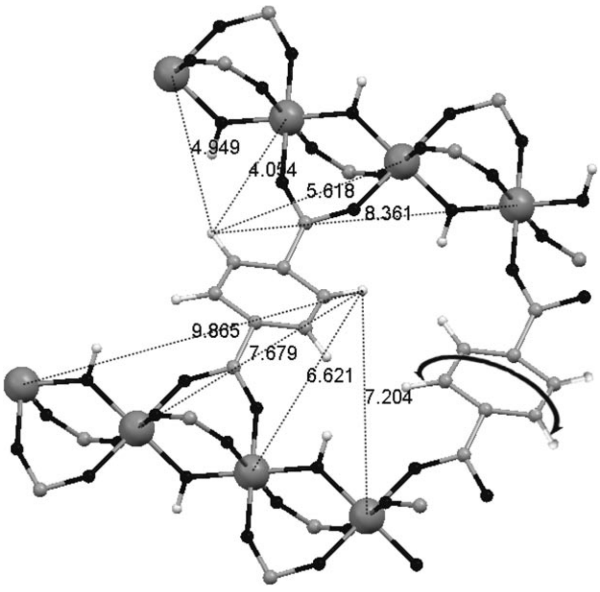

Figure 2. View of the MIL-53(Cr) structure fragment used to derive geometry information for dipolar interaction; distances are given in Å. On the right, the aromatic ring performs a π flip about its C_2 symmetry axis.

In the case of quadrupole interaction, the evolution of the spectral line shape reflects averaging of the interaction tensor due to the angular motion of the C–D bond. For the aromatic rings in the selected MILs, three types of motion can be expected: π flips around the C_2 symmetry axis, continuous free diffusion around the same axis, and restricted libration in a sector.[25] Comparison between the experimental and calculated line shapes (Figures 3 and 4) demonstrates that in both MIL-47(V) and MIL-53(Cr), π flipping occurs. In both cases, the line shape consists of a single component, static below 300 K and steadily changing on heating above room temperature. The temperature dependence of the π-flip rate shows that it is a normal Arrhenius process (Figure 5). For MIL-47(V) the flipping rate constant k is characterized by an activation energy $E_V = 45\,\mathrm{kJ\,mol^{-1}}$ and a pre-exponential factor $k_{V0} = 0.88 \times 10^{11}\,\mathrm{s^{-1}}$, while for MIL-53(Cr) $E_{Cr} = 41\,\mathrm{kJ\,mol^{-1}}$ and $k_{Cr0} = 1.26 \times 10^{11}\,\mathrm{s^{-1}}$. The rate and activation barrier for the torsional dynamics of the organic linkers thus depend on the different geometries and electronic structures around the two metal ions, although hydrogen bonding of the type OH···O(carboxylate) cannot be rejected. The sensitivity of the aromatic ring as a local structural marker becomes even more evident if one compares these results with experimental data on MOF-5. Our activation energies are similar to that obtained for MOF-5,[18] but in both MILs the flipping rate at the same temperature is at least one order of magnitude slower, which is reflected in the smaller pre-exponential

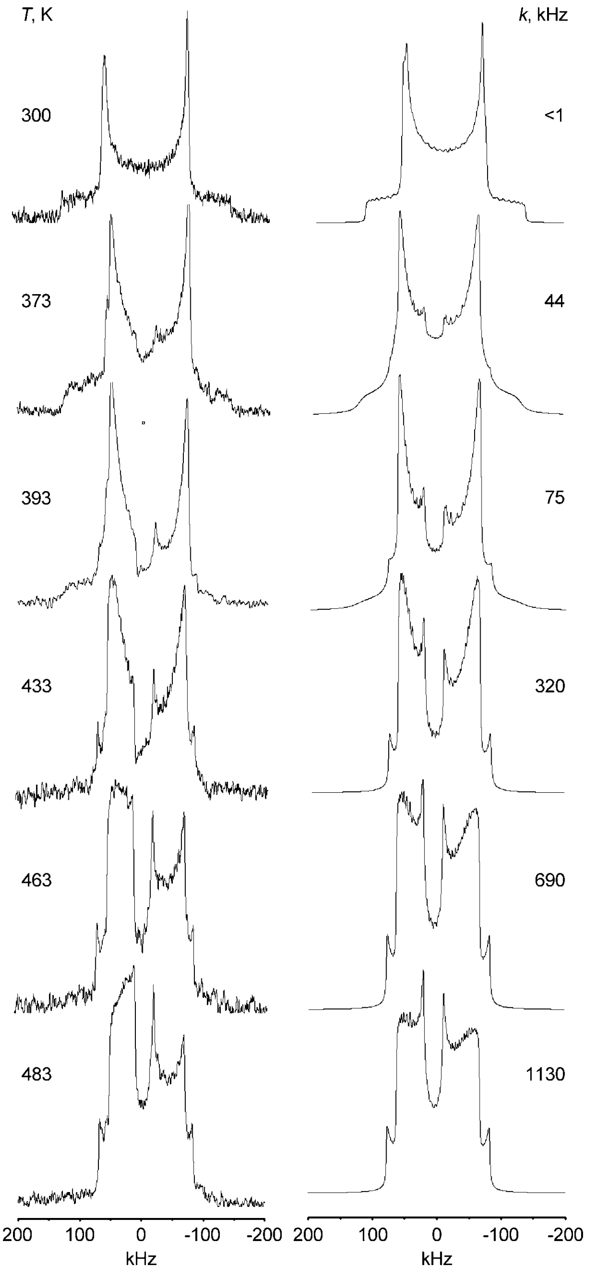

Figure 3. Experimental (left column) and simulated (right column) ^{2}H NMR temperature dependence of the spectral line shape of the aromatic rings in MIL-47(V); k is the π-flip rate constant.

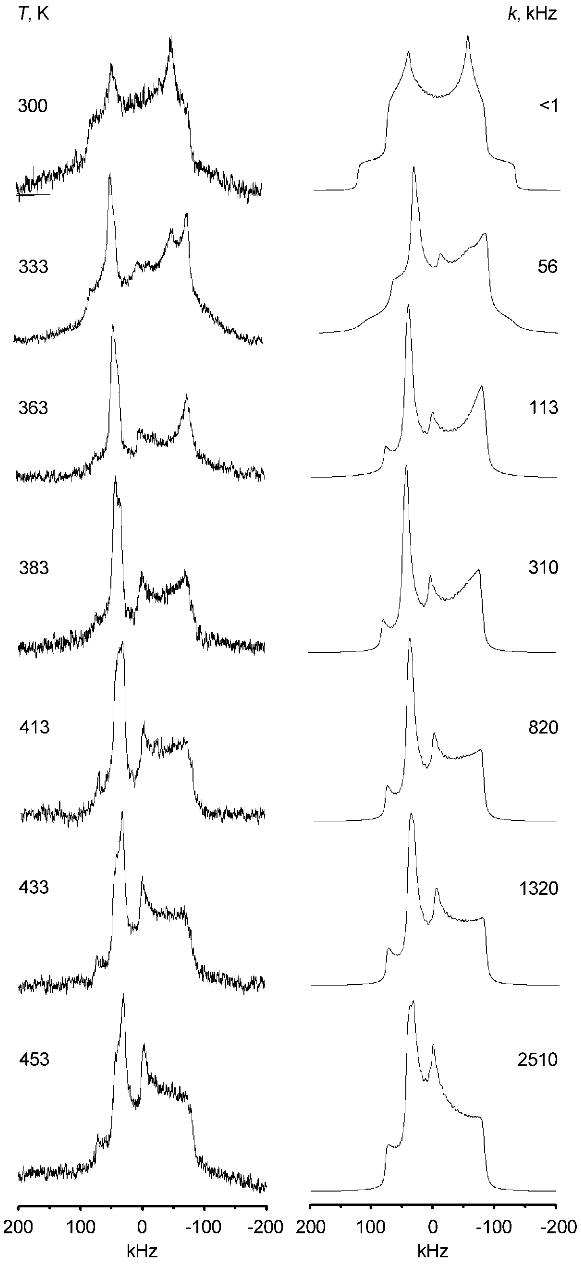

Figure 4. Experimental (left column) and simulated (right column) ^{2}H NMR temperature dependence of the spectra line shape of the aromatic rings in MIL-53(Cr): k is the π-flip rate constant.

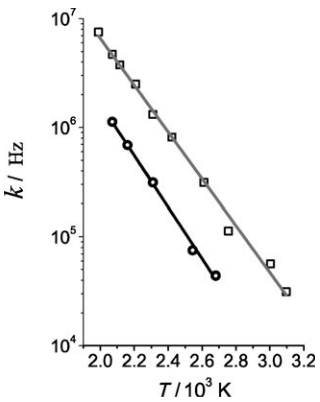

Figure 5. Arrhenius plot of the flipping rate constant in MIL-47(V) (○) and MIL-53(Cr) (□).

factors. This difference could reflect the rather constrained local environment for the phenylene ring in a 1D pore system (MIL-47 and −53) when compared to a 3D one (MOF-5).

At temperatures below 300 K, the aromatic rings are static in both MILs, and the static quadrupole interaction tensor is characterized by $Q_0 \approx 170$ kHz and $\eta = 0$, which are typical values for a C−D bond in an aromatic ring.[25] While relatively straightforward for MIL-47(V), these values are not trivial for MIL-53(Cr). The difference lies in the strength of dipolar interaction, which in the case of MIL-53 is about five times stronger, so that the presence of eight neighboring paramagnetic sites creates an almost symmetrical distortion of the initial static ^{2}H NMR spectrum.

Although the dipolar interaction becomes stronger at low temperatures (ca. $1/T$), the spectral line shape for MIL-47(V) remains almost unchanged, and shows only this relatively weak effect. For MIL-53(Cr), the situation is more complex; on slow cooling, the structure progressively changes towards the NP phase, as already observed for the Al analogue.[12] This structural change shrinks the unit cell and brings the Cr^{3+} ions closer, so that eight nearest in-plane centers are not sufficient to describe the dipolar interaction, and additional out-of-plane ions should be taken into account, even if their influence is smaller. In principle, this effect can be used to follow the phase transition phenomenon occurring in the material, but for a detailed simulation, precise distances between ^{2}H and out-of plane Cr ions are required.

In conclusion, the ^{2}H NMR method allowed us to unveil that the aromatic rings in MIL-47(V) and MIL-53(Cr) perform π flips about their symmetry axis. The benzene rings flip faster and with lower activation energy in the flexible MIL-53(Cr) than in the rigid MIL-47(V). This demonstrates that aromatic rings in MOFs can be a sensitive marker of the framework structural properties. The terephthalate groups in both MILs can be considered as immobile on a microscopic timescale, in agreement with previous QENS studies and molecular simulations.[19–21] However, in macroscopic measurements, small molecules like H_2, CO_2, and CH_4 have the possibility to switch from one tunnel to another, and this must be taken into account, for instance, in adsorption or separation processes.

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[1] H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276.
[2] S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem.* **2004**, *116*, 2388; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334.
[3] D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior, M. J. Rosseinsky, *Acc. Chem. Res.* **2005**, *38*, 273.
[4] G. Férey, *Chem. Soc. Rev.* **2008**, *37*, 191.
[5] D. Farrusseng, S. Aguado, C. Pinel, *Angew. Chem.* **2009**, *121*, 7638; *Angew. Chem. Int. Ed.* **2009**, *48*, 7502.
[6] G. Férey, C. Serre, *Chem. Soc. Rev.* **2009**, *38*, 1380.
[7] C. Serre, F. Millange, C. Thouvenot, M. Noguès, G. Marsolier, D. Louër, G. Férey, *J. Am. Chem. Soc.* **2002**, *124*, 13519.
[8] K. Barthelet, J. Marrot, D. Riou, G. Férey, *Angew. Chem.* **2002**, *114*, 291; *Angew. Chem. Int. Ed.* **2002**, *41*, 281.
[9] P. L. Llewellyn, G. Maurin, T. Devic, S. Loera-Serna, N. Rosenbach, C. Serre, S. Bourelly, P. Horcajada, Y. Filinchuk, G. Férey, *J. Am. Chem. Soc.* **2008**, *130*, 12808.
[10] C. Serre, S. Bourrely, A. Vimont, N. A. Ramsahye, G. Maurin, P. L. Llewellyn, M. Daturi, Y. Filinchuk, O. Leynaud, P. Barnes, G. Férey, *Adv. Mater.* **2007**, *19*, 2246.
[11] A. Boutin, M. A. Springuel-Huet, A. Nossov, A. Gédéon, T. Loiseau, C. Volkringer, G. Férey, F. X. Coudert, A. Fuchs, *Angew. Chem.* **2009**, *121*, 8464; *Angew. Chem. Int. Ed.* **2009**, *48*, 8314.
[12] Y. Liu, J. H. Her, A. Dailly, A. J. Ramirez-Cuesta, D. A. Neumann, C. M. Brown, *J. Am. Chem. Soc.* **2008**, *130*, 11813.
[13] W. Zhou, T. Yildirim, *Phys. Rev. B* **2006**, *74*, 180301.
[14] M. Tafipolsky, S. Amirjalayer, R. Schmid, *J. Comput. Chem.* **2007**, *28*, 1169.
[15] J. A. Greathouse, M. D. Allendorf, *J. Phys. Chem. C* **2008**, *112*, 5795.
[16] H. Jobic, D. N. Theodorou, *Microporous Mesoporous Mater.* **2007**, *102*, 21.
[17] J. Gonzalez, R. N. Devi, D. P. Tunstall, P. O. Cox, P. A. Wright, *Microporous Mesoporous Mater.* **2005**, *84*, 97.
[18] S. L. Gould, D. Tranchemontagne, O. M. Yaghi, M. A. Garcia-Garibay, *J. Am. Chem. Soc.* **2008**, *130*, 3246.
[19] F. Salles, H. Jobic, G. Maurin, M. M. Koza, P. L. Llewellyn, T. Devic, C. Serre, G. Férey, *Phys. Rev. Lett.* **2008**, *100*, 245901.
[20] N. Rosenbach, H. Jobic, A. Ghoufi, F. Salles, G. Maurin, S. Bourrelly, P. L. Llewellyn, T. Devic, C. Serre, G. Férey, *Angew. Chem.* **2008**, *120*, 6713; *Angew. Chem. Int. Ed.* **2008**, *47*, 6611.
[21] F. Salles, H. Jobic, A. Ghoufi, P. L. Llewellyn, C. Serre, S. Bourrelly, G. Férey, G. Maurin, *Angew. Chem.* **2009**, *121*, 8485; *Angew. Chem. Int. Ed.* **2009**, *48*, 8335.
[22] M. Mizuno, N. Itakura, K. Endo, *Chem. Phys. Lett.* **2005**, *416*, 358.
[23] S. Antonijevic, S. *J.* Wimperis, *Magn. Reson.* **2003**, 164, 343.
[24] R. J. Wittebort, E. T. Olejniczak, R. G. Griffin, *J. Chem. Phys.* **1987**, *86*, 5411.
[25] L. W. Jelinski in *High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk (Methods and Stereochemical Analysis)*, *Vol. 7* (Ed.: R. A. Komoroski), VCH Publishers, New York, **1986**, p. 335.