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COMMUNICATION

Chiral recognition in metal–organic frameworks studied by solid-state NMR spectroscopy using chiral solvating agents†

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Recently, we have described the synthesis of chiral metal–organic frameworks *i*Pr-ChirUMCM-1 and Bn-ChirUMCM-1 and their use in enantioselective separation. Here, we demonstrate for the first time the use of a chiral solvating agent (1-phenyl-2,2,2-trifluoroethanol, TFPE) for chiral recognition in *i*Pr-ChirUMCM-1 and Bn-ChirUMCM-1 by means of solid-state ¹³C NMR spectroscopy.

Metal–Organic Frameworks (MOFs)^{2–4} are hybrid materials formed by organic and inorganic building blocks.⁵ The interactions between organic and inorganic constituents are relatively strong⁶ resulting in three-dimensional network structures.⁵ Often, these networks exhibit micro- or mesopore systems of huge internal surface area.⁷ Applications of MOFs are envisioned in catalysis,^{8–12} gas storage,¹⁰ for gas and solvent purification,^{13–15} and as nano reactors.³ They may also be useful as highly selective molecular sieves, sensors,^{16–21} in microelectronics,²² and for optical purposes. In addition, chiral MOFs are currently gaining research interest for enantioselective separation and catalysis. Recently, we have described the synthesis of chiral analogues of the metal–organic framework UMCM-1 (University of Michigan Crystalline Material-1) and their application in enantioselective separation.¹

Magnetic resonance spectroscopy is frequently used for the characterization of porous materials and their interactions with adsorbed species (host–guest interactions). For example, ¹H, ¹³C, ²⁷Al, and ³¹P magic angle spinning (MAS) nuclear magnetic resonance (NMR),^{23–30} diffusion measurements by pulsed field gradient³¹ NMR, ¹²⁹Xe NMR,^{32,33} and electron paramagnetic resonance spectroscopy^{34,35} were previously applied to study MOFs. Here, we describe the solid-state NMR spectroscopic characterization of MOFs with respect to their

chiral properties. *Ad hoc*, NMR is unable to discriminate different enantiomers of chiral compounds. However, liquid-state NMR offers approaches to detect chirality of dissolved molecules, *e.g.*, via their interaction with intrinsically chiral, ordered systems such as liquid crystals or with so-called chiral shift agents.^{36–42} If enantiomerically pure chiral shift agents are used, the substrate enantiomers can be distinguished through the formation of non-equivalent diastereomeric complexes. Chiral derivatizing agents form covalent bonds. Chiral solvating agents associate non-covalently with the substrate. The resulting complexes can be differentiated by NMR, *e.g.*, via their different complexation-induced chemical shift changes. These differences are usually small, *i.e.*, of the order of 0.1–1 ppm for ¹³C.⁴⁰ Skogsberg *et al.*⁴³ studied chiral separation of enantiomers by high-performance liquid chromatography using a chiral stationary phase as well as by NMR spectroscopy. Compared to liquid-state NMR spectroscopy, solid-state NMR has only found a limited number of applications for chirality studies yet. Gajda *et al.*⁴⁴ applied ³¹P solid-state NMR to study enantioselective inclusion complexation. Porto *et al.*⁴⁵ described resin-bound chiral derivatizing agents for the assignment of molecular configuration by high-resolution MAS NMR spectroscopy. So far, chiral shift agents were limited to liquid-state NMR where the line widths are low enough to measure the above-described small effects. In contrast, solid-state NMR spectra often exhibit line widths of several ppm. However, the solid-state ¹³C NMR spectra of numerous metal–organic frameworks are extremely well resolved. This is particularly true for UMCM-1 and its chiral derivatives (see Fig. 1 and ESI† Fig. S2 and S3).¹

In the present communication, we show for the first time the use of the chiral solvating agent 1-phenyl-2,2,2-trifluoroethanol (TFPE)^{37,38} for chiral recognition in MOFs by solid-state ¹³C NMR spectroscopy. TFPE was chosen because it is known to interact with C=O groups, *e.g.*, of lactones.³⁷ Furthermore, the relatively small TFPE molecule fits well into the large mesopores as well as into the smaller pores containing the chiral side groups in chirally modified UMCM-1 (ChirUMCM-1). UMCM-1⁴⁶ and its chiral, enantiomerically pure derivatives^{1,47} *i*Pr-ChirUMCM-1 (*i*Pr = isopropyl) and Bn-ChirUMCM-1 (Bn = benzyl) were synthesized as described previously (Fig. S1, ESI†) and loaded as described in ESI.† Initial experiments were carried out on unmodified, achiral UMCM-1 which

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† Electronic supplementary information (ESI) available: Fig. S1: schematic representation of synthesis procedure, Fig. S2: ¹³C CP MAS NMR spectra of achiral UMCM-1, Fig. S3: ¹³C CP MAS NMR spectra of Bn-ChirUMCM-1, Fig. S4: ¹³C CP MAS NMR spectra of Bn-ChirUMCM-1 (selected regions). See DOI: 10.1039/c2cc35366k

Fig. 1 ^{13}C CP MAS NMR spectra of *iPr*-ChirUMCM-1. Top (red): sample loaded with (*R*)-TFPE. Middle (blue): sample loaded with (*S*)-TFPE. Bottom (black): unloaded sample. The structure of the modified BDC-linker (Chir-BDC) bearing the chiral side group is shown in the figure in order to define the carbon positions of the assigned signals. Stars denote signals due to TFPE.

crystallizes in a non-chiral space group $P6_3/m$ (no. 176). As expected, the ^{13}C CP MAS NMR spectra of the achiral MOF loaded with (*R*)- and (*S*)-TFPE are identical (Fig. S2, ESI†). Loading with TFPE results in changes of the UMCM-1-spectra indicating strong host–guest interactions and/or adsorption-induced changes of the mobility. However, these changes are identical for both TFPE-enantiomers. The signals of TFPE are clearly visible in ^{13}C CP MAS NMR spectra of the loaded UMCM-1 samples.

This would not be observed for pure liquid TFPE due to the isotropic motions of the molecules. The presence of carbon signals due to TFPE indicates a significant immobilization of the TFPE molecules by interactions with the hosts UMCM-1 and ChirUMCM-1.

Loading of both chiral MOFs with the different TFPE-enantiomers results in significant changes of the spectra. The ^{13}C CP MAS NMR spectra of *iPr*-ChirUMCM-1 in the activated, unloaded state as well as after loading with equal amounts of the two different enantiomers (*R*)-/(*S*)-TFPE are shown in Fig. 1. The carbon signals due to the chiral side groups – which are broad and almost undetectable in unloaded samples¹ – become clearly visible in loaded samples. The signals of carbon atoms 1–6 located at the chiral side group/linker are assigned. In the unloaded sample, the two signals due to C1 are only weak and broad and the signals due to C2–C5 are practically invisible. This effect is due to dynamical disorder of the mobile chiral side groups.¹ Appearance of these signals after loading is caused by the interaction of the chiral side groups with TFPE resulting in a better defined and/or less mobile state. Comparison of the spectra loaded with (*R*)- and (*S*)-TFPE reveals different chemical shifts for selected signals. Pronounced differences of the order of 0.1–0.4 ppm are observed for the signals due to C1 and C5 located at the chiral side group, *i.e.*, near the stereochemical center and for signals due to the carboxylate group (C6) of the Chir-BDC-linker (see Fig. 2). The center of gravity of the signal due to the side group C=O

Fig. 2 Selected regions from the ^{13}C CP MAS NMR spectra of *iPr*-ChirUMCM-1 loaded with (*R*)-TFPE (red curves) and (*S*)-TFPE (blue curves). Top: chiral side group C=O (C5); middle: side group signals due to carbon atom C1; bottom: linker carboxylate signals.

(C5, Fig. 2, top) exhibits a shift difference of 0.4 ppm for the two enantiomers.

Moreover, the C6-signals (Chir-BDC-linker carboxylate, Fig. 2, bottom) also show clear chemical shift differences for loading with the two different enantiomers. In contrast, the carboxylate signal at *ca.* 177 ppm due to the achiral benzene-1,3,5-tribenzoate-linker (BTB-linker) occurs at the same position for (*R*)- and (*S*)-TFPE-loading. This observation shows that the different TFPE-enantiomers interact identically with the achiral linkers. Analogous experiments on the chiral MOF Bn-ChirUMCM-1 (Fig. S3 and S4, ESI†) revealed a similar behavior which confirms the described observations.

In summary, the use of chiral shift agents allows chiral recognition in metal–organic frameworks by solid-state NMR spectroscopy as has been shown for *iPr*-ChirUMCM-1 and Bn-ChirUMCM-1 using enantiomerically pure (*R*)-/(*S*)-TFPE. Pronounced chemical shift differences were observed exclusively for carbon atoms located in the modified, chiral BDC-linkers. Interactions between the chiral BDC-linkers and enantiomerically pure (*R*)- or (*S*)-TFPE result in the formation of NMR-distinguishable complexes with different chemical shifts which can be measured due to the excellent spectral resolution of the ^{13}C CP MAS NMR spectra.

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Notes and references

- 1 M. Padmanaban, P. Müller, C. Lieder, K. Gedrich, R. Grunker, V. Bon, I. Senkovska, S. Baumgärtner, S. Opelt, S. Paasch, E. Brunner, F. Glorius, E. Klemm and S. Kaskel, *Chem. Commun.*, 2011, **47**, 12089.

- 2 S. Kitagawa, R. Kitaura and S.-i. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334.
- 3 G. Férey, *Stud. Surf. Sci. Catal.*, 2007, **170**, 66.
- 4 S. Kaskel, *Handb. Porous Solids*, 2002, **2**, 1190.
- 5 G. Férey, *Dalton Trans.*, 2009, 4400.
- 6 J. L. C. Rowsell and O. M. Yaghi, *Microporous Mesoporous Mater.*, 2004, **73**, 3.
- 7 G. Férey, *Chem. Soc. Rev.*, 2008, **37**, 191.
- 8 A. U. Czaja, N. Trukhan and U. Müller, *Chem. Soc. Rev.*, 2009, **38**, 1284.
- 9 L. Ma, C. Abney and W. Lin, *Chem. Soc. Rev.*, 2009, **38**, 1248.
- 10 S. Proch, J. Herrmannsdörfer, R. Kempe, C. Kern, A. Jess, L. Seyfarth and J. Senker, *Chem.-Eur. J.*, 2008, **14**, 8204.
- 11 A. Henschel, K. Gedrich, R. Kraehnert and S. Kaskel, *Chem. Commun.*, 2008, **35**, 4192.
- 12 J. Y. Lee, O. Farha, J. T. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450.
- 13 L. Hamon, C. Serre, T. Devic, T. Loiseau, F. Millange, G. Férey and G. D. Weireld, *J. Am. Chem. Soc.*, 2009, **131**, 8775.
- 14 J. A. Greathouse, T. L. Kinniburgh and M. D. Allendorf, *Ind. Eng. Chem. Res.*, 2009, **48**, 3425.
- 15 J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477.
- 16 T. M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley and O. M. Yaghi, *J. Am. Chem. Soc.*, 1999, **121**, 1651.
- 17 B. D. Chandler, A. P. Čoté, D. T. Cramb, J. M. Hill and G. K. H. Shimizu, *Chem. Commun.*, 2002, 1900.
- 18 G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray and J. D. Cashion, *Science*, 2002, **298**, 1762.
- 19 D. Maspoch, D. Ruiz-Molina, K. Wurst, N. Domingo, M. Cavallini, F. Biscarini, J. Tejada, C. Rovira and J. Veciana, *Nat. Mater.*, 2003, **2**, 190.
- 20 M. D. Allendorf, R. J. T. Houk, L. Andruszkiewicz, A. A. Talin, J. Pikarsky, A. Choudhury, K. A. Gall and P. J. Hesketh, *J. Am. Chem. Soc.*, 2008, **130**, 14404.
- 21 C. Serre, C. Mellot-Draznieks, S. Surblé, N. Audebrand, Y. Filinchuk and G. Férey, *Science*, 2007, **315**, 1828.
- 22 J. A. Real, E. Andrés, M. C. Muñoz, M. Julve, T. Granier, A. Bousseksou and F. Varret, *Science*, 1995, **268**, 265.
- 23 M. Müller, O. I. Lebedev and R. A. Fischer, *J. Mater. Chem.*, 2008, **18**, 5274.
- 24 E. Y. Lee, S. Y. Jang and M. P. Suh, *J. Am. Chem. Soc.*, 2005, **127**, 6374.
- 25 A. Comotti, S. Bracco, P. Sozzani, S. Horike, R. Matsuda, J. Chen, M. Takata, Y. Kubota and S. Kitagawa, *J. Am. Chem. Soc.*, 2008, **130**, 13664.
- 26 M. Haouas, C. Volkringer, T. Loiseau, G. Férey and F. Taulelle, *Chemistry*, 2009, **15**, 3139.
- 27 P. Silva, F. Vieira, A. C. Gomes, D. Ananias, J. A. Fernandes, S. M. Bruno, R. Soares, A. A. Valente, J. Rocha and F. A. Paz, *J. Am. Chem. Soc.*, 2011, **133**, 15120.
- 28 F. Gul-E-Noor, B. Jee, A. Pöpl, M. Hartmann, D. Himsl and M. Bertmer, *Phys. Chem. Chem. Phys.*, 2011, **13**, 7783.
- 29 J. J. Gassensmith, H. Furukawa, R. A. Smaldone, R. S. Forgan, Y. Y. Botros, O. M. Yaghi and J. F. Stoddart, *J. Am. Chem. Soc.*, 2011, **133**, 15312.
- 30 A. J. Rossini, A. Zagdoun, M. Lelli, J. Canivet, S. Aguado, O. Ouari, P. Tordo, W. E. Maas, C. Copéret, D. Farusseng, L. Emsley and A. Lesage, *Angew. Chem., Int. Ed.*, 2012, **51**, 123.
- 31 F. Stallmach, S. Gröger, V. Künzel, J. Kärger, O. M. Yaghi, M. Hesse and U. Müller, *Angew. Chem.*, 2006, **118**, 2177.
- 32 M.-A. Springuel-Huet, A. Nossou, Z. Adem, F. Guenneau, C. Volkringer, T. Loiseau, G. Férey and A. Gédéon, *J. Am. Chem. Soc.*, 2010, **132**, 11599.
- 33 H. C. Hoffmann, B. Assfour, F. Epperlein, N. Klein, S. Paasch, I. Senkovska, S. Kaskel, G. Seifert and E. Brunner, *J. Am. Chem. Soc.*, 2011, **133**, 8681.
- 34 Y. Jiang, J. Huang, B. Kasumaj, G. Jeschke, M. Hunger, T. Mallat and A. Baiker, *J. Am. Chem. Soc.*, 2009, **131**, 2058.
- 35 B. Jee, K. Eisinger, F. Gul-E-Noor, M. Bertmer, M. Hartmann, D. Himsl and A. Pöpl, *J. Phys. Chem. C*, 2010, **114**, 16630.
- 36 D. Parker, *Chem. Rev.*, 1991, **91**, 1441.
- 37 T. J. Wenzel, *Discrimination of Chiral Compounds Using NMR Spectroscopy*, Wiley, Hoboken, NJ, 2007.
- 38 T. J. Wenzel and C. D. Chisholm, *Prog. Nucl. Magn. Reson. Spectrosc.*, 2011, **59**, 1.
- 39 T. J. Wenzel and C. D. Chisholm, *Chirality*, 2011, **23**, 190.
- 40 T. J. Wenzel and J. D. Wilcox, *Chirality*, 2003, **15**, 256.
- 41 P. Lesot, O. Lafon, H. Zimmermann and Z. Luz, *J. Am. Chem. Soc.*, 2008, **130**, 8754.
- 42 C. Aroulanda, H. Zimmermann, Z. Luz and P. Lesot, *J. Chem. Phys.*, 2011, **134**, 134502.
- 43 U. Skogsberg, H. Händel, D. Sanchez and K. Albert, *J. Chromatogr., A*, 2004, **1023**, 215.
- 44 J. Gajda, A. Jeziorna, W. Cieselski, W. M. Potrzebowski, W. W. Prezdo and M. J. Potrzebowski, *Solid State Nucl. Magn. Reson.*, 2007, **31**, 153.
- 45 S. Porto, J. M. Seco, J. F. Espinosa, E. Quinoa and R. Riguera, *J. Org. Chem.*, 2008, **73**, 5714.
- 46 K. Koh, A. G. Wong-Foy and A. J. Matzger, *Angew. Chem., Int. Ed.*, 2008, **47**, 677.
- 47 Y. Gnani and F. Glorius, *Synthesis*, 2006, 1899.