Exploring zinc-terephthalate complexes through multi nuclear ssNMR and *in-situ* reaction monitoring by Raman spectroscopy

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Mechanochemistry has shown impressive improvements in past decades for developing sophisticated materials such as pharmaceutical cocrystals, zeolite-based catalysts or metal-organic frameworks (MOFs). [1] The latter are elaborate porous materials exhibiting interesting applications in storage of fuels, capture of CO_2, catalysis... [2] Being able to control the nature of MOFs synthesized under mechanochemical conditions thus appears as an important goal. In this context, recently, *in-situ* methods for mechano-synthesis, such as X-Ray diffraction under synchrotron beam or Raman spectroscopy, have emerged so that information about reaction rates and presence of intermediates are now becoming accessible. [3]

In this contribution, we have studied the formation of zinc-based MOFs using terephthalic acid as organic ligand. The observation of several intermediate phases was made possible by *in-situ* Raman spectroscopy during ball-milling synthesis (see Fig. 1 a)). Solid-state NMR spectroscopy was then used, along with FTIR, to obtain information about unknown structures observed during the synthetic route. ^{13}C chemical shifts were proven to be sensitive to the binding mode of the dicarboxylic acids on the zinc atoms, in line with previous studies. [4] Chemical shift differences up to 5 ppm (Fig. 1 b)) helped to distinguish between monodentate and bridging binding modes. Moreover, further structural information could be obtained using ^{17}O NMR studies of enriched compounds.

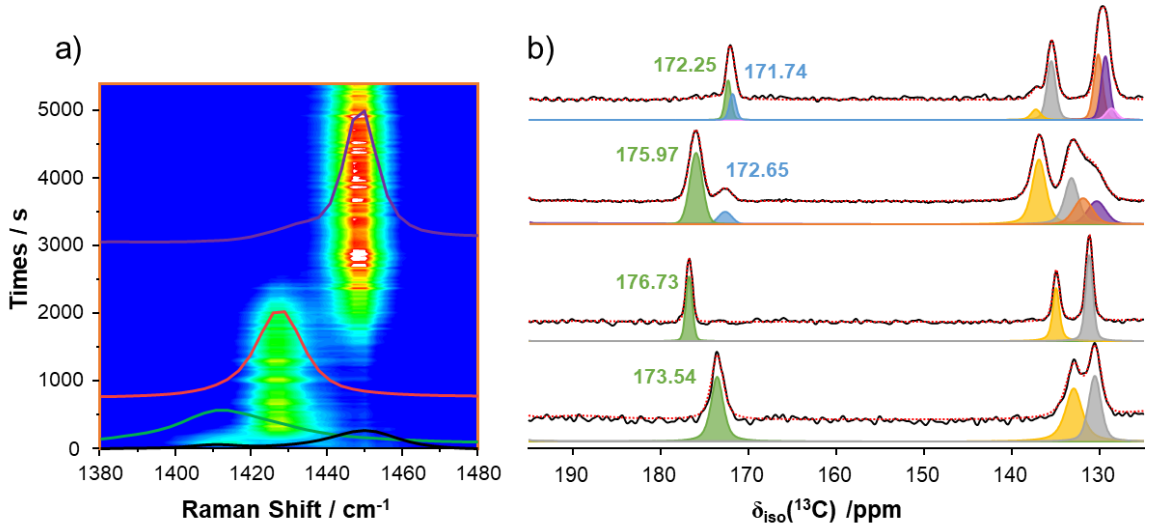

Figure 1. a) *In-situ* Raman spectroscopy of zinc terephthalates coordination complexes. b) ^{13}C ssNMR of the four different phases observed with Raman spectroscopy during the ball-milling synthesis.

[1] Friščić, T., Mottillo, C. & Titi, H. M. (2020). *Angew. Chem. Int. Ed.* **59**, 1018-1029.

[2] Furukawa, H., Cordova, K. E., O'Keeffe, M. & Yaghi, O. M. (2013). *Science.* **341**, 1230444.

[3] Kulla, H., Haferkamp, S., Akhmetova, I., Röllig, M., Maierhofer, C., Rademann, K. & Emmerling, F. (2018). *Angew. Chem. Int. Ed.* **57**, 5930-5933.

[4] Habib, H. A., Hoffmann, A., Höppe, H. A. & Janiak, C. (2009). *Dalton. Trans.* **10**, 1742-1751.

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