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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 CO₂, 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. ¹³C 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 ¹⁷O NMR studies of enriched compounds.

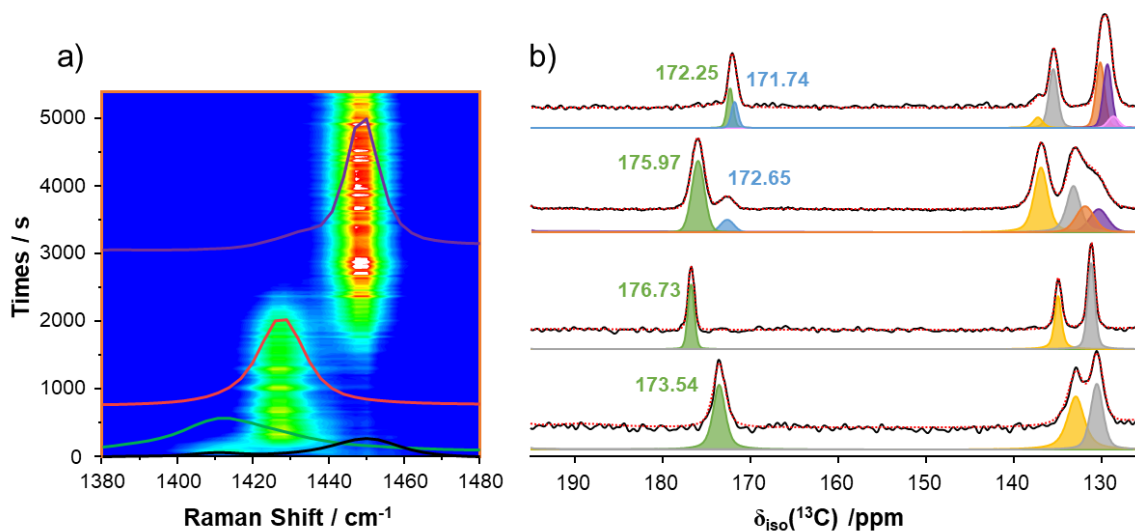


Figure 1. a) *In-situ* Raman spectroscopy of zinc terephthalates coordination complexes. b) ¹³C ssNMR of the four different phases observed with Raman spectroscopy during the ball-milling synthesis.

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