

Microsymposium

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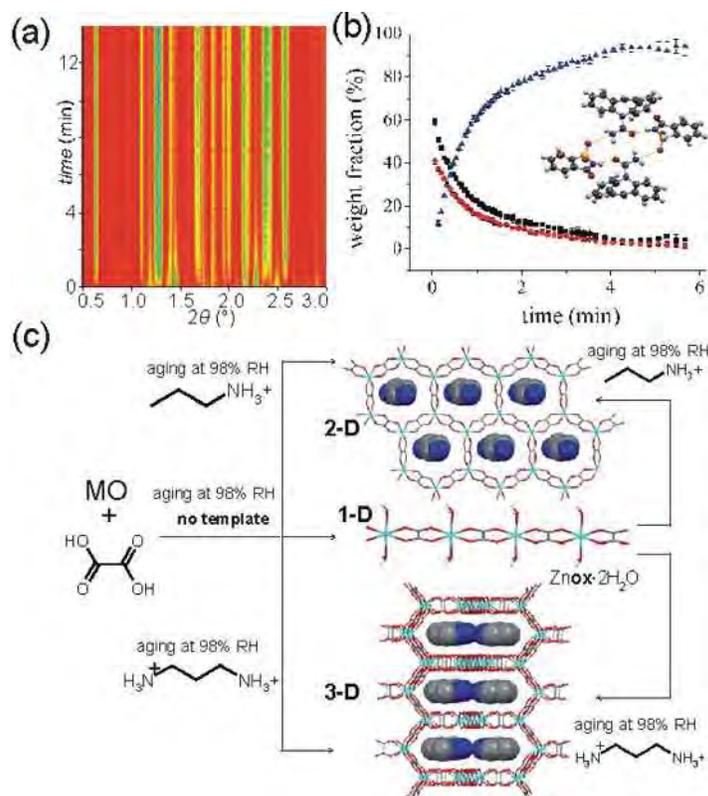
Solid-state assembly of metal-organic architectures

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Chemical reactions induced or sustained by mechanical force (mechanochemistry) have attracted considerable interest as a means to achieve cleaner and "greener" solvent-free synthesis of molecules and materials. Such reactions also provide an opportunity to explore molecular recognition and self-assembly without the interfering effects of bulk solvents, such as solubility, complexation with solvent, or solvolysis.[1] This presentation will highlight our recent exploration of solvent-free chemistry as a means to understand the assembly, templating and the collapse of porous metal-organic structures. First, the recently developed methodology for real-time, in situ monitoring of mechanochemical reactions will be presented,[2] which uses highly penetrating synchrotron radiation to directly observe chemical and structural transformations during mechanical milling. By using this methodology it was possible, for the first time, to illuminate the mechanisms of metal-organic framework formation by milling, and observe new, fleeting intermediate phases. The second part of the presentation will focus on 'accelerated aging", a simple, diffusion-controlled and catalytically-accelerated methodology for the transformation of inert metal oxides into metal-organic architectures under the conditions mimicking those of geological mineral "weathering".[3] This solvent-free and low-energy technique provides reactant generality not yet demonstrated in mechanochemistry, and allows the transformations of diverse transition, main group and lanthanide metal oxides, into 2- and 3-dimensional metal-organic architectures. The applications of accelerated aging in the clean synthesis of metal-organic frameworks and low-energy, solvent-free mineral separation will be discussed.

[1] T. Friščić, *Chem. Soc. Rev.*, 2012, 41, 3493., [2] T. Friščić, I. Halasz, P. J. Beldon, et al., *Nature Chem.*, 2013, 5, 66., [3] M. J. Cliffe, C. Mottillo, R. S. Stein, et al., *Chem. Sci.*, 2012, 3, 2495.



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