

## Ionic Liquids as Substrates for Metal-Organic Framework Synthesis

**Authors :** Julian Mehler, Marcus Fischer, Martin Hartmann, Peter S. Schulz

**Abstract :** During the last two decades, the synthesis of metal-organic frameworks (MOFs) has gained ever increasing attention. Based on their pore size and shape as well as host-guest interactions, they are of interest for numerous fields related to porous materials, like catalysis and gas separation. Usually, MOF-synthesis takes place in an organic solvent between room temperature and approximately 220 °C, with mixtures of polyfunctional organic linker molecules and metal precursors as substrates. Reaction temperatures above the boiling point of the solvent, i.e. solvothermal reactions, are run in autoclaves or sealed glass vessels under autogenous pressures. A relatively new approach for the synthesis of MOFs is the so-called ionothermal synthesis route. It applies an ionic liquid as a solvent, which can serve as a structure-directing template and/or a charge-compensating agent in the final coordination polymer structure. Furthermore, this method often allows for less harsh reaction conditions than the solvothermal route. Here a variation of the ionothermal approach is reported, where the ionic liquid also serves as an organic linker source. By using 1-ethyl-3-methylimidazolium terephthalates ([EMIM][Hbdc] and [EMIM]<sub>2</sub>[bdc]), the one-step synthesis of MIL-53(Al)/Boehemite composites with interesting features is possible. The resulting material is already formed at moderate temperatures (90-130 °C) and is stabilized in the usually unfavored ht-phase. Additionally, in contrast to already published procedures for MIL-53(Al) synthesis, no further activation at high temperatures is mandatory. A full characterization of this novel composite material is provided, including XRD, SS-NMR, EI-Al., SEM as well as sorption measurements and its interesting features are compared to MIL-53(Al) samples produced by the classical solvothermal route. Furthermore, the syntheses of the applied ionic liquids and salts is discussed. The influence of the degree of ionicity of the linker source [EMIM]<sub>x</sub>[H(2-x)bdc] on the crystal structure and the achievable synthesis temperature are investigated and give insight into the role of the IL during synthesis. Aside from the synthesis of MIL-53 from EMIM terephthalates, the use of the phosphonium cation in this approach is discussed as well. Additionally, the employment of ILs in the preparation of other MOFs is presented briefly. This includes the ZIF-4 framework from the respective imidazolates ILs and chiral camphorate based frameworks from their imidazolium precursors.

**Keywords :** ionic liquids, ionothermal synthesis, material synthesis, MIL-53, MOFs

**Conference Title :** ICAIL 2018 : International Conference on Advances in Ionic Liquids

**Conference Location :** Venice, Italy

**Conference Dates :** April 12-13, 2018