

Main-Group Elements in Coordination Polymers for Energy Applications

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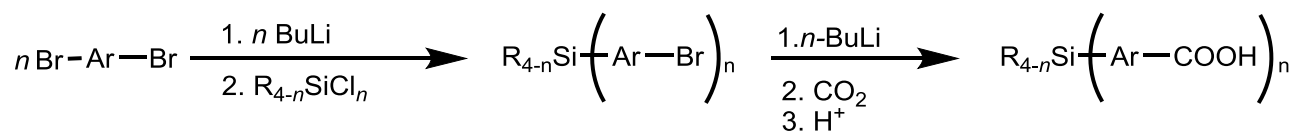
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Abstract

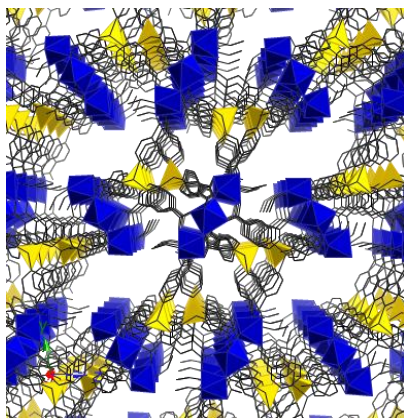
Metal-organic frameworks (MOFs) are porous polymers in which metal centres are linked via polydentate organic linkers. They have become widely studied in recent years due to their potential in many areas such as energy, CO₂ capture, catalysis, and drug delivery. These applications rely on the ability of the size, shape and chemical nature of the pores in MOFs to be tailored by suitable choice of both the metal and the organic linker. The use of main group metals as either the nodes in the polymer or as components of the linkers has been explored far less than transition metals as the nodes with well known organic linkers. The aim of this work was to demonstrate that group 1 and 2 elements may be used as nodes to prepare interesting MOFs and that organosilicon linkers can be used to give novel coordination polymers.

In group 2, Mg²⁺ nodes can be used to replace Zn²⁺ in MOFs derived from aromatic linkers such as linear 1,4-benzenedicarboxylic acid (H₂bdc), 4,4-biphenyldicarboxylic acid (H₂bpdc) and trigonal planar 1,3,5-tricarboxylic acid (H₃btc) [1] and Si²⁺ forms a polymeric chain with [(*p*-CO₂HC₆H₄)Me₂Si]₂O. In group 1, Li⁺ and Na⁺ both form complicated polymers with organosilicon linkers such as (*p*-CO₂HC₆H₄)₃SiMe.

A wide range of useful polydentate organosilicon linkers for application in coordination polymer synthesis have been prepared using a convenient synthetic route involving simple chloro- or alkoxy-silane precursors *i.e.*:



This synthetic method enables simple compounds such as R_nSi(*p*-C₆H₄CO₂H)_{4-n} (n = 0, 1, or 2; R = Me, Et, Ph *etc.*) as well as more complicated linkers such as C₆H₄-*p*-[(SiC₆H₄CO₂H)₃]₂ to be prepared [2, 3]. Related silicon-based tetrazolate linkers can be prepared from nitrile precursors prepared using a similar route to the carboxylic acids [4]. These novel linkers can be used to prepare a wide range of MOFs that have been studied for both CO₂ capture and for hydrogen storage. For example, reaction between Si(*p*-C₆H₄CO₂H)₄ and Co(NO₃)₂ affords a porous MOF, see below, capable of hydrogen uptake [5]. This MOF, together with other MOFs containing Si linkers, will be described.



A view down the x-axis of the MOF formed from Si(*p*-C₆H₄CO₂H)₄ and Co(NO₃)₂

Keywords: Metal-Organic Framework, hydrogen storage, organosilicon, main-group elements.

References:

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