

Tuning Proton Conductivity in A Multifunctional Calcium Phosphonate Hybrid Framework

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Multi-chelating phosphonate ligands are organic linkers alternative to polycarboxylates and other ligands providing synthetic access to a number of thermally- and chemically-stable MOFs [1]. Metal phosphonates are amenable for accessing suitable and highly conducting materials both by tuning structural features and post-synthesis treatment [2,3]. For instance, proton conductivity values in the order of 10^{-2} S cm⁻¹ have been reported for several phosphonate-based compounds [4].

We report hereby the synthesis, structural characterization and proton conductivity of an open framework hybrid, Ca₂[(HO₃PC₆H₃COOH)₂](HO₃PC₆H₃(COO)₂H)(H₂O)₂]·5H₂O, that combines Ca²⁺ ions and the rigid polyfunctional ligand 5-(dihydroxyphosphoryl)isophthalic acid. This compound was obtained by slow crystallization at ambient conditions at pH ~3. Its complex pillared layered structure, solved by single crystal X-ray analysis, contains hydrophilic 1D channels filled with both water and acidic phosphonate and carboxylate groups creating a hydrogen-bonded network. Partial removal of the lattice water at 75 °C causes a monoclinic structural distortion but still retaining the initial conductivity properties ($5.7 \cdot 10^{-4}$ S·cm⁻¹). Exposure of the sample to ammonia vapor from a concentrated aqueous solution led to major structural changes resulting in a new layered material containing seven NH₃ and sixteen H₂O molecules per formula. This solid exhibits enhanced conductivity, reaching $6.6 \cdot 10^{-3}$ S·cm⁻¹, as measured at 98 % RH and T = 24 °C. Activation energies were between 0.23 and 0.40 eV, typical of a Grothuss mechanism of proton conduction.

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