Syntheses and polymorphic transformations of ionic crystals based on mononuclear bismuth(III) complexes and polyoxometalates

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Keywords: ionic crystal; polymorphism; bismuth ion; polyoxometalate; proton transport

The controlled assembly of molecules, ions, and ligands as building blocks based on crystal engineering leads to various functional crystalline solids. In particular, polyoxometalates (POMs), which are anionic metal oxide clusters, have been a popular motif in crystal engineering[1)]. To revisit simple mononuclear metal complexes as counter cations of POMs, seven ionic crystals based on Keggin- or Dawson-type POMs with mononuclear bismuth(III) complexes[2),3)] as counter cations were synthesized (Fig. 1). The bismuth(III) center exhibited triangular dodecahedron, square antiprism, or pseudo-cubic eight-coordination geometries, with dimethyl sulfoxide or *N*,*N*-dimethylformamide as ligands. The ionic crystals showed polymorphic transformation depending on the synthetic or recrystallization conditions. As a method for exploring functionality, proton conductivities of the ionic crystals were measured under humidified conditions. The ionic crystals with high porosity, tertiary amine moieties, or coordination water exhibited high proton conductivities, and large activation energies indicate that protons are transferred mainly with water molecules via vehicle mechanism[4)].

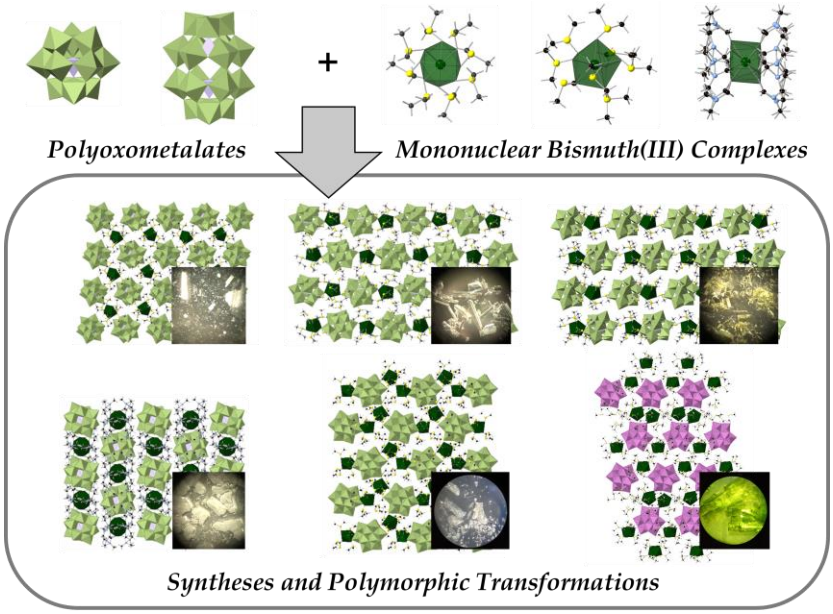

Fig. 1 Ionic crystals based on polyoxometalates and mononuclear bismuth(III) complexes

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