Piezo-solvatomorphism of iHOF — a porous, hydrogen bond-assisted ionic organic framework

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Hydrogen bond-assisted ionic organic frameworks (iHOFs)[1] represent an emerging class of porous organic materials characterized by the ability to form porous three-dimensional aggregates stabilized by charge-assisted hydrogen bonds and anion···π interactions. These frameworks have attracted growing attention due to their broad application potential in drug delivery,[2] adsorption, heterogeneous catalysis,[3] molecular storage[4] and many more.[5] While polymorphism and solvatomorphism have been widely investigated in porous materials, pressure-induced solvatomorphism remains relatively underexplored and offers new perspectives for modulating the structural and functional properties of such compounds.

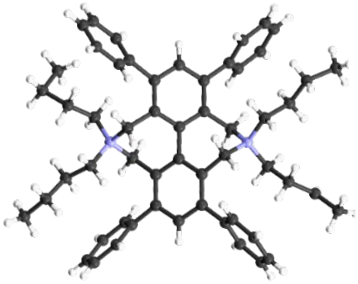

Fig. 1 The iHOF molecule present in iHOF·xMeOH at 0.55 GPa, bromine anions and methanol molecules omitted for clarity.

We report the piezo-solvatomorphism[6] of an iHOF observed through *in situ* isochoric recrystallizations from methanol and water under high-pressure. Remarkably, despite the general tendency of pressure to promote closely packed crystal structure, all high-pressure isochoric recrystallization experiments consistently yielded porous framework structures. Recrystallization from methanol resulted in two forms of iHOF·*n*MeOH that differ in guest methanol content: the low-pressure structure, stable up to 0.4 GPa crystallizing in the triclinic space group $P\overline{1}$, and a higher-pressure form, stable above 0.4 GPa adopting a tetragonal $P4_2/n$ space group (Fig. 1). Similarly, recrystallization from water led to two forms of the iHOF hydrate (iHOF·xH$_2$O), also differing in guest content: a low-pressure tetragonal structure stable up to approx. 0.2 GPa, and a high-pressure structure crystallizing in the cubic space group $Ia\overline{3}d$. As observed before for $[H_3O][PbI_3]\cdot nH_2O$ obtained at high-pressure, compression can lead to the desorption of small, co-crystallized, guest molecules,[7] which aligns with the reduced void volume observed in both iHOF·*n*MeOH and iHOF·xH$_2$O.

These results underscore the complex relationship between molecular flexibility, solvation effects, and supramolecular interactions in governing the structural aggregation of three-dimensional frameworks at high pressure. The demonstrated examples show a huge perspective for the application of high-pressure in exploring novel topologies of complex framework materials.

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