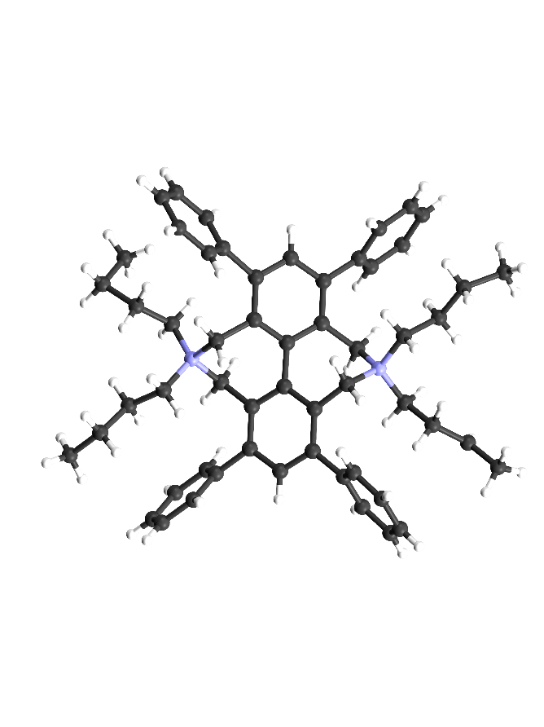
## Piezo-solvatomorphism of iHOF — a porous, hydrogen bond-assisted ionic organic framework

## G. Russ1, T. Holczbauer2,3, S. De2, P. Bombicz2, A. Katrusiak1, S. Sobczak1

1Department of Materials Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Poznan; 2Centre for Structural Research, HUN-REN research Centre for Natural Sciences, Budapest, Hungary; 3Institute of Organic Chemistry, Research Centre for Natural Sciences, H-1117 Budapest, Magyar Tudósok körútja 2.

### 1grarus@st.amu.edu.pl

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 , and a higher-pressure form, stable above 0.4 GPa adopting a tetragonal *P*42/*n* space group (Fig. 1). Similarly, recrystallization from water led to two forms of the iHOF hydrate (iHOF·*x*H₂O), also differing in guest content: a low-pressure tetragonal structure stable up to approx. 0.2GPa, and a high-pressure structure crystallizing in the cubic space group *Iad*. As observed before for [H3O][PbI3]·*n*H2O 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·*x*H₂O.

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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