Moving Metal-Organic Frameworks in Different Directions: Liquids, Glasses, Composites and *PT* Phase Diagrams

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Metal-organic frameworks (MOFs) are microporous materials with huge potential as host structures for chemical processes, including retention, catalytic reaction, or separation of guest molecules. Structural collapse at high-pressure, and unusual behaviours at elevated temperatures, such as melting and transitions to liquid states, have recently been observed in the family.[1, 2] Here, we discuss not only the mechanism of melting and the structure of the resultant glasses, but we also show that the effect of the application of simultaneous high-pressure and -temperature on a MOF can be understood in terms of silicate analogues, with crystalline, amorphous and liquid states occurring across the pressure - temperature phase diagram. The responses of ZIF-4, and ZIF-62, the MOFs on which we focus, to simultaneous pressure and temperature reveals a complex behaviour with distinct high- and low- density amorphous phases, crystalline polymorphs and liquid states occurring over different regions of the pressure-temperature space.[3, 4]

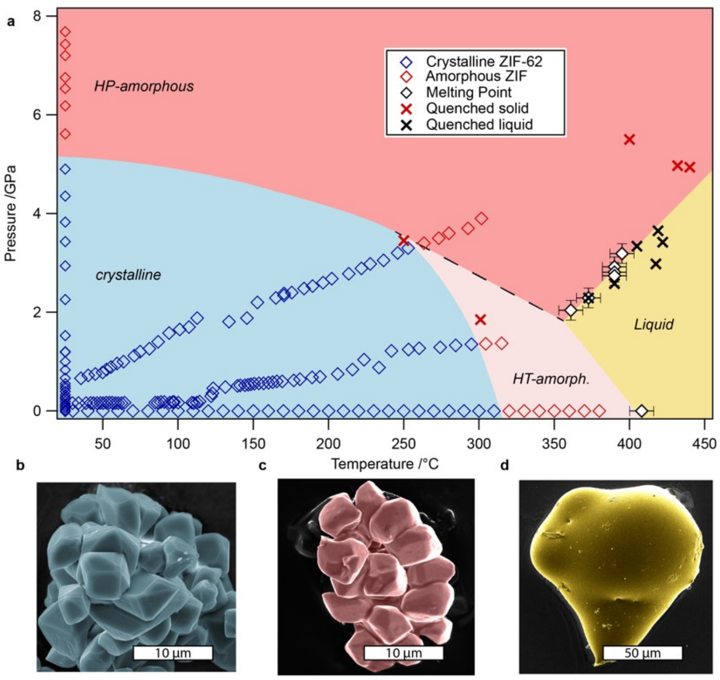

Figure 1. Experimentally derived P-T phase diagram for ZIF-62

a, The stability fields for crystalline ZIF-62 (blue), amorphous (red) and liquid (yellow). The phase-field for liquid ZIF-62 is defined by melting points (black diamonds) observed optically at high-pressure and using DSC at ambient pressure. Crosses indicate high-pressure/high-temperature conditions from which the samples were quenched for morphological analysis. **b, c,** and **d,** Scanning-electron microscopic images of the three main phases of ZIF-62.

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