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Inorganic-organic hybrid glass formation

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Scientists have recently discovered that some of both the metal-organic framework (MOF) materials and metal coordination polymer (MCP) can be melted and vitrified upon quenching.¹⁻³ The thus-derived glass is here referred to as the inorganic-organic hybrid glass, i.e., the glass hybridized between metal atoms and organic molecules. MOFs and MCPs are porous 3D frameworks of exceptional interest for gas storage and separation, catalysis and drug delivery. Since the MOFs are synthesized as powder, they are impossible to be processed to films and bulk objects with different geometries. However, the melting behavior of some MOFs or MCPs enables doing so. Here, we present some progress in understanding the melting and vitrifying behaviors of two types of MOFs, namely, ZIF-4 and ZIF-62. ZIF refers to zeolitic imidazolate framework, which is a subset of MOFs with zeolitic structures. We show some striking results concerning the high sensitivity of the melting and glass transition behaviors of ZIF-4 and ZIF-62 to chemical tuning and synthesis conditions, and clarify the origin of such sensitivity. We also present some perspectives and challenges in upscaling production of bulk MOF glasses. Compared to conventional glasses, the newly discovered hybrid glasses have unique mechanical properties compared to those of organic and inorganic glasses. We demonstrate the fascinating indentation behavior of ZIF-62 glass, which is in strong contrast to other types of glasses. Besides practical importance, the study of MOF glass is of scientific significance. We report on the calorimetric signature of the polyamorphic transition and recrystallization in ZIF-4.

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