Metal-Organic Framework Liquids and Glasses

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Abstract

Metal–organic frameworks (MOFs) are a family of chemically diverse materials, consisting of inorganic nodes or ions linked by organic ligands. They have applications in a wide range of fields, covering engineering, physics, chemistry, biology and medicine. Until recently, research has focused almost entirely on crystalline structures, with over 60,000 structures now known. However, now a clear trend is emerging, shifting the emphasis onto disordered states, including 'defective by design' crystals, as well as amorphous phases such as glasses.
We have recently shown a subset of metal-organic frameworks (MOFs), called zeolitic imidazolate frameworks (ZIFs), to melt, and quenching of the resultant liquids forms a new category of glass.1 Several structures (e.g. ZIF-4 [Zn(C3H3N2)2]) melt between 400 and 600 ◦C, and the glasses obtained upon cooling retain the short-range order (i.e. local bonding under 6 Å) present in their crystalline counterparts.2

Here, we introduce the concept of a *liquid metal-organic framework*,3 and explore the mechanism of melting of ZIF-4, via *in-situ* pair distribution function measurements and associated Reverse Monte-Carlo modelling, coupled with density functional theory based molecular dynamics calculations. We show that melting proceeds with significant structural retention, due to breakage of only part of the metal coordination sphere. The structure of the liquid phase is characterized, as is the mechanism of vitrification upon cooling. The atomic configuration obtained bears striking similarities to that for *a*SiO2.

1. Bennett, Coudert et al, *Nat. Chem.*, **2017**, 9, 11-16.
2. Bennett* et al, *Nat. Commun.,* **2015**, 6, 8079.
3. Gaillac, Keen, Beyer, Chapman, Bennett* and Coudert*, *Nat. Mater.,* **2017**, 16, 1149-1154.

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