Nature Reviews Materials | Published online 31 Oct 2017; doi:10.1038/natrevmats.2017.74

METAL–ORGANIC FRAMEWORKS

Molten MOFs

> Liquid MOFs… have value as intermediates to obtain MOF glasses, enabling the shaping and casting of macroscopic architectures

Metal–organic frameworks (MOFs), to most of us, are ordered solids, and little is known about MOF liquids and glasses. Now, reporting in *Nature Materials*, Thomas Bennett, François-Xavier Coudert and colleagues have combined experiment and theory to investigate the melting behaviour and liquid state of MOFs.

"MOFs have changed the way that we see porous materials," says Coudert. "But despite their rich chemistry and versatile geometries, they are still seen as rigid, perfect, crystalline frameworks." However, there is now growing interest in exploring amorphous solid, gel and melt-quenched glass forms of MOFs. In particular, the liquid phase has only recently been identified.

The researchers investigate the melting of ZIF-4, which comprises tetrahedral Zn^{2+} nodes linked by bidentate imidazolate bridges, and establish that liquid ZIF-4 is a rare example of an intrinsically porous liquid — a 'MOF liquid'. When crystalline ZIF-4 is heated above its melting point (~865 K) and then cooled to room temperature, a melt-quenched glass is obtained. On heating to 856 K, the structural changes in this glass, as observed by X-ray diffraction, are consistent with the formation of a liquid.

Results from first-principles molecular dynamics simulations were in excellent agreement with the experimental observations. Moreover, analysis of the coordination number of Zn^{2+} in the simulations shows that tetracoordinate metal centres persist in the liquid — albeit with increased motion of the atoms and dynamic exchange of the Zn–N coordinative bonds — indicating that the chemical nature of the liquid is similar to that of the solid.

On characterizing the dynamics of the liquid, the team found the diffusion of the cations and anions to be strongly correlated, a phenomenon often observed for ionic liquids. But it is the porosity of liquid ZIF-4 that is its most intriguing feature: the computed estimates suggest that much of the porosity of the solid is retained in the liquid, which is more porous than the glass.

Porous liquids may be advantageous for certain applications, such as industrial-scale gas separation. "Liquid MOFs also have value as intermediates to obtain MOF glasses, enabling the shaping and casting of macroscopic architectures with mechanical properties superior to those of crystalline powders," says Coudert. Importantly, the researchers predict that liquids could potentially be obtained for other families of MOFs. "Both the thermal decomposition and melting points can be altered, and different methods used to produce the liquid state, which will be important in generalizing this phenomenon," explains Bennett.

However, further work is needed to understand the relationship between liquid MOFs and the properties of the resultant glassy MOFs, and to establish how MOF liquids differ from their solid-state analogues and other related materials. Indeed, the strongly associated nature and preferred tetrahedral coordination of the liquid MOF is reminiscent of liquid water. Thus, Coudert muses that this study also poses more fundamental questions: "does this MOF liquid behave like a normal liquid, or is it likely to share with water some of its anomalies?"

Bennett hopes that this study will inspire scientists to think differently about MOFs and to establish connections between the field of MOFs and those of ionic liquids and glasses.

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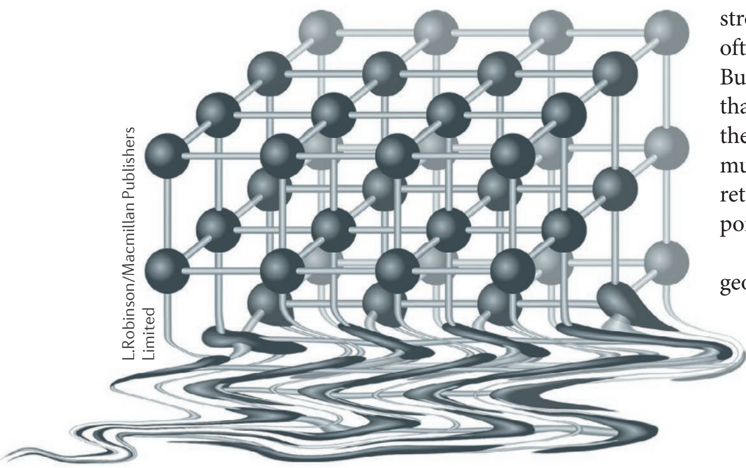

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ORIGINAL ARTICLE Gaillac, R. *et al.* Liquid metal–organic frameworks. *Nat. Mater.* https://dx.doi.org/10.1038/nmat4998 (2017)