

Exploring the formation of Hf metal-organic frameworks

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Metal-organic frameworks (MOFs) are of great interest for applications such as energy storage and carbon capture [1] and have outstanding chemical tunability.[2] In particular, the isostructural Zr and Hf MOFs are particularly promising for real-world applications due to their stability.[3] We recently discovered that the formation during synthesis of Hf metal clusters with different nuclearities and geometries results in a dramatic change in the structure of the subsequent MOF. Selection between the resultant MOF phases can be controlled by tuning the synthesis conditions, including temperature and solvent system. [4,5,6] This finding raises the possibility of designing syntheses to obtain previously inaccessible MOF phases with new metal clusters and therefore different reactive properties. While recent studies have demonstrated the importance of understanding the formation of MOF frameworks, [7,8] the evolution of their formation, from individual clusters and their precursors through to the ordering of the full framework, during the reaction must be fully explored and understood in order to rationally synthesise new MOFs.

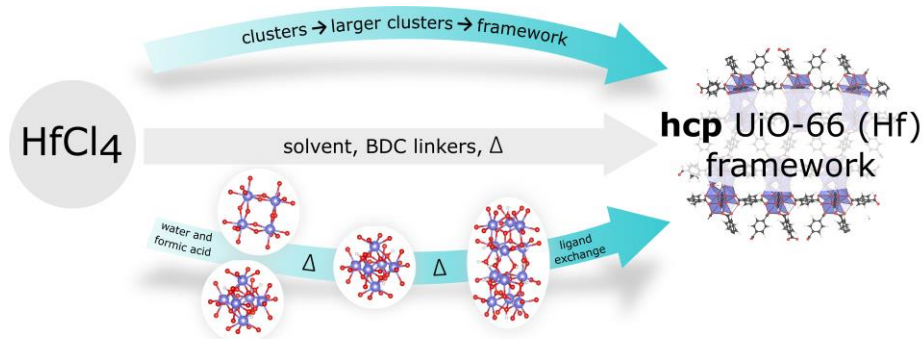


Figure 1. Schematic of hcp UiO-66(Hf) MOF formation through different cluster intermediates.

In our previous work, we have shown that X-ray Pair Distribution Function (XPDF) measurements are sensitive to the identity of the cluster in Zr MOFs, and can clearly distinguish between isolated Zr atoms, Zr₆ clusters, and Zr₁₂ clusters.[5] Here we show that XPDF measurements, taken *in situ* during reactions of both Hf precursor solutions and the full hcp UiO-66(Hf) MOF, can be used to identify critical intermediates in the materials,[9] improving our understanding of stages of growth of Hf metal-organic frameworks [Figure 1] and hence providing routes towards the efficient design of syntheses for new and unrealised members of this important MOF family.

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