

## Multi-facetted dynamic behaviour of a flexible metal-organic framework through post-synthetic modification

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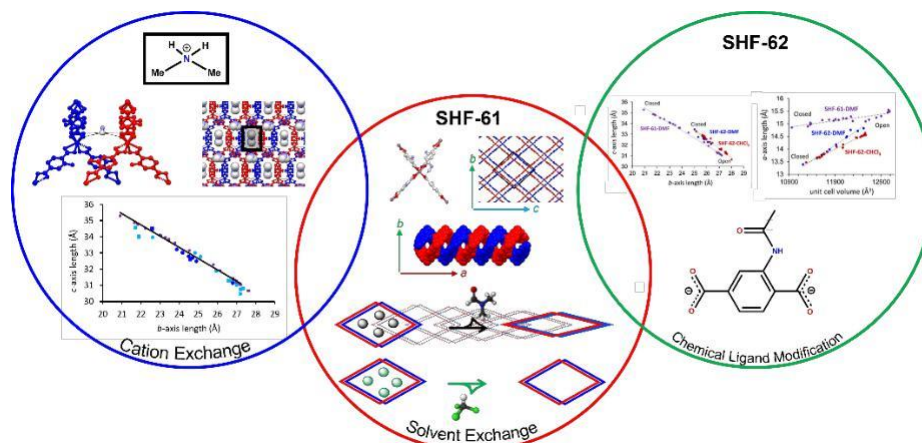
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Metal-organic frameworks (MOFs) are constructed from inorganic coordination nodes and multi-topic organic linkers to form a regular repeating network. These polymeric materials possess large solvent-filled voids, which are often retained upon solvent removal, making MOFs attractive for applications involving adsorption and release of small molecules (e.g. gas separation). In recent years, however, it has been shown that a growing number of these materials undergo dynamical structural changes upon removal or inclusion of guest molecules. Such dynamic behaviour is often enabled by flexibility of ligands or coordination geometry and can result from a response to a variety of stimuli, such as temperature, pressure and guest content. To fully understand and harness the dynamic behaviour a combination of diffraction, other physical measurements and computational techniques are required.

In recent years we have extensively explored one such flexible MOF material, SHF-61,[1] which comprises indium metal nodes connected with aminoterephthalate linkers into a doubly interpenetrated anionic diamondoid framework, the charge being balanced by mobile cations within the pores. Initial studies demonstrated a continuous solvent-dependent *two-dimensional* breathing behaviour (pore-width changes).[1] Subsequent post-synthetic modification of the organic linker to convert amino groups to amides (SHF-62) unlocked a *three-dimensional* flexible response upon solvent (pore-width and pore-length changes).[2] Most recently we have identified a third means of framework modification through replacement of the mobile cation within the pores of the framework. This has allowed evaluation of the effect of cation size and intermolecular interactions on the dynamic range of the material and has highlighted the key role of the cation in the dynamic response of this family of MOF materials.

This presentation will demonstrate that through three means of post-synthetic modification (solvent exchange, ligand modification and cation replacement, Figure 1) it has been possible to develop comprehensive picture of the large-amplitude continuous dynamic behaviour in the framework SHF-61 and its related family of MOFs. All materials have been characterised extensively by SCXRD and PXRD methods, including *in situ* diffraction studies during pore-solvent removal and gas adsorption, using both laboratory data and synchrotron data from Diamond Light Source. The diffraction studies are complemented by a variety of other characterisation methods and mechanistic understanding is enhanced by adsorption studies and computational modelling.

The ability to apply three different post-synthetic modification methods presents a unique opportunity to not only control the flexibility but also potentially tailor the guest inclusion properties and applications of this versatile material.



**Figure 1.** Overview of the three modifications for SHF-61

[1] Carrington E.J., McAnally C. A., Fletcher A. J., Thompson S. P., Warren M., Brammer L. (2017). *Nat. Chem.*, **9**, 882-889.

[2] Carrington E. J., Dodsworth S. F., van Meurs S., Warren M. R., Brammer L. (2021). *Angew. Chem. Int. Ed.*, **60**, 17920-17924.

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