Design and Application of Porous Materials

Developing the application of the crystalline sponge method

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The crystalline sponge (CS) method made waves in the scientific community when first published in 2013. [1] It removes the necessity of sample crystallisation for single crystal X-ray diffraction (SCXRD) by utilising the crystallinity and porosity of metal organic frameworks (MOFs). However, adoption of the technique has been primarily limited to the pharmaceutical industry and academic work has rarely strayed outside of original authors' laboratories. Our work seeks to showcase the suitability of the CS method to the wide diversity of chemistry undertaken in academia and further develop understanding of the technique as a standard analytical tool.

Initial research has explored a family of novel biaryl molecules sourced from a synthetic organic laboratory at the University of Southampton. Characterisation experiments have resulted in elucidation of the molecular structure of 13 synthetic oils via SCXRD, illustrated below in Fig. 1, and represents the first systematic compound library generated by CS research. [2] The systematic structural differences provide a range of comparable data to investigate host···guest and guest···guest interactions. Our analysis provides insights into analyte preferences for intermolecular interactions through consideration of steric and electronic effects. These fundamental observations also provide preliminary insight into the mechanism by which the stable host-guest complexes form.

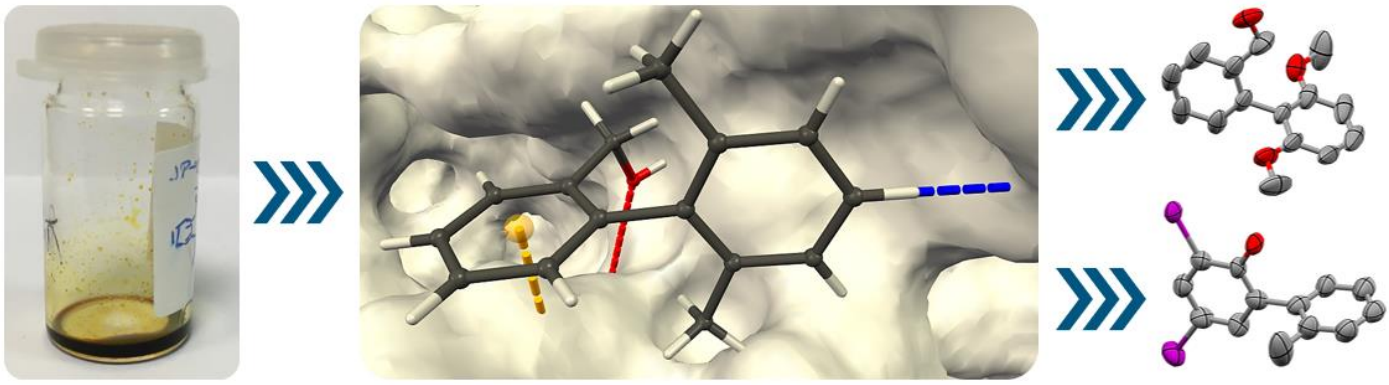

Figure 1. Representative 'oil to structure' procedure for biaryl alcohols utilising the CS method.

Since its first publication, there has been the prospect 'solution-state' SCXRD data due to the conformational freedom of guests within the framework cavities. Our work is now progressing onto classification of the pore environment experienced by analyte molecules and the conformational restraints imposed by the system. This will be achieved by additional analysis combining solution state spectroscopy and computational modelling. To further complement this analysis, classical SCXRD data of analyte molecules is being sought. The oily nature and difficulty of crystallisation, which initially made these materials of interest to study, will be combatted with advanced crystallisation techniques, particularly encapsulated nanodroplet crystallisation (ENaCt), a high-throughput method for obtaining single crystals of organic-soluble small molecules. [3] Through combination of these analytical techniques, a 'spectrum' of conformational flexibility is being constructed which ranges from the freedom of the gas phase to the highly constrained classical crystal system. Geometric comparisons of analytes then provide detail on the level of influence from the host framework and allow for guest conformational freedom to be plotted on this spectrum.

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[2] Harrowven, D.C., Pearce, J.E., Coles, S.J., Carroll, R.C. (2023). *[In Preparation]*

[3] Tyler, A.R., Ragbirsingh, R., McMonagle, C.J., Waddell, P.G., Heaps, S.E., Steed, J.W., Thaw, P., Hall, M.J., Probert, M.R. (2020). *Chem*, **6**, 1755-1765.