Poster

Mechanochemical synthesis and structural characterization of hexaflurosilicate containing MOFs

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Metal-organic frameworks (MOFs) are highly diverse polymeric materials, which are formed by strong covalent bonds between the selected metal nodes and organic linkers. It has been demonstrated in numerous instances where MOFs are excellent for gas separation applications [1] and the hexafluosilicate (SIFSIX) MOFs are among them. The three-dimensional framework of SIFSIX MOFs is constructed by metal nodes and the two-dimensional linker sheets pillared with $SiF6^{2-}$ anions. The exact functionality of the SIFSIX MOF is strictly related to the node-and-linker composition. Traditionally, solution crystallization or solvothermal techniques have been employed to obtain various SIFSIFX MOFs. Herein, the alternative green chemistry-driven mechanochemical synthesis methods were applied to obtain the porous Zn(II)-based SIFSIX MOF [2]. Moreover, a series of post synthesis thermal induced phase transformations have been investigated, where a variety of computational and experimental approaches were devoted to solving a newly discovered phase.

The liquid-assisted grinding (LAG) method was used to obtain Zn(**bipy**)$_2$SiF$_6$, which initially yielded a non-porous interpenetrated phase [3]. In order to acquire the porous Zn(**bipy**)$_2$SiF$_6$ polymorph, the water-containing interpenetrated phase was stored under high temperature to encourage phase transformations. In the post synthesis thermal studies, a previously unreported phase was observed. After attempting to solve the structure directly from powder X-ray measurement (PXRD) data, the *ab initio* crystal structure prediction [4] method developed in our group was employed. However, due to the limitation of high computational cost from all periodic density functional theory (DFT) calculations, the alternative electron diffraction (ED) measurements were performed. Through ED measurements, tensive structure of the unknown phase was revealed. Overall, this work has highlighted the applicability of applying the more environment-friendly mechanochemical approach to synthesis SIFSIX MOFs in contrast to the conventional solution-based crystallisation techniques, with the aid of a wide range of experimental and computational methods for the determination of unknown structures.

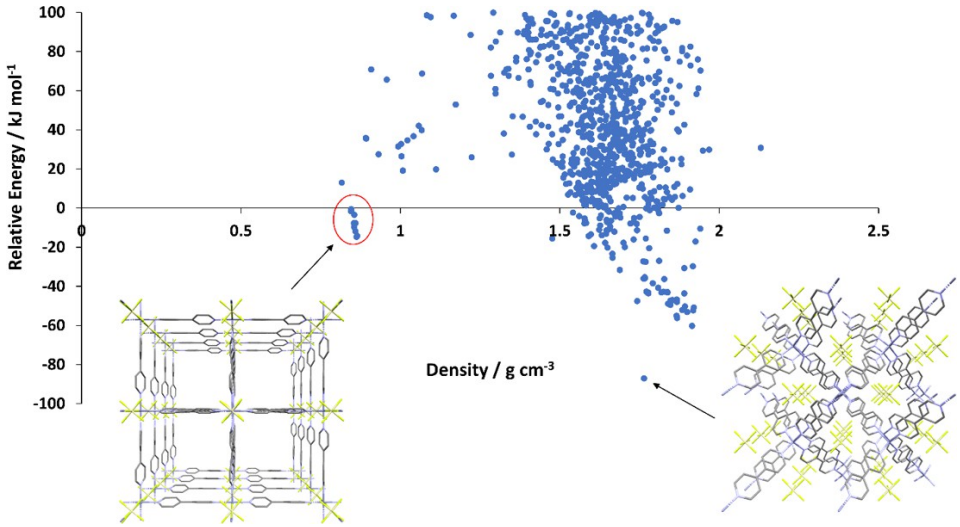

Figure 1. Calculated energy landscape of Zn(**bipy**)$_2$SiF$_6$ structures. The structure of the global minimum is shown while the dots circled in red are representing the experimental matching porous phase.

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